John's AMS Instrument Development

- Hardware/Upgrades/Development
- Upgrades
- Adjustable lens system
- 16 mm quad
- Differentially pumped ionizer/quad region
- Alcatel hybrid pump
- Channel apertures
- Porous conical heater with thermocouple
- Redesigned electronics boxes/reduced cabling
- Inlet pressure gauge for sample flow

Performance Upgrades

- List of instruments delivered
- Upgrades
- High emission current ionizer
  - Balzers IS420 signals increase linearly up to 8mA, tungsten lifetime decreases
  - Reduced volume ionizer
  - 2x increase in NO3 IE, selectively improves plume ionization
  - Closed source ionizer, tested 50% increase in IE
  - photo
  - Ionizer Magnets, tested, 2x increase in IE but also increases single particle pulse width, decreases the size resolution (plot). Spirals electrons in the ionizer, increasing the interaction time. Effect of broadening (~2X) is not as bad with the small volume ionizer. Chopper width is still more important in broadening the TOF SP signal.

High Emission Current Operation

- IPP vs. emission current plot, with AB and IE, tungsten signal also increases. W, IPP, AB, and IE all increase with emission current. Lifetime is very short with higher current. Looking into 2% thoriated tungsten filaments, but no apparent reduction in tungsten signal with the thoriated (alloy vs. surface coating?). Final: haven't gotten there yet.

Summary of Ionizer Enhancements

- Closed ionizer, IPP = 400 (signal increase)
- Small volume ionizer, IPP =800 (S/N increase)
- Magnets, IPP =2000 (but impact on size resolution)
- High emission current ionizer, IPP =8000+ (dynamic range limited)
  - Need to evaluation S/N increase

Performance Upgrades

- High throughput lens, designed, needs to be built, requires V301
- Converging inlet, tested to increase transmission of larger particles
- Conversion dynode, tested Balzers SEV218, mass bias eliminated, but ion collection efficiency reduced.
- Restek (glass) coating on detection cylinder, implemented, not yet quantified, may reduce water and organic background.

Upgrade Plots Summary

- Converging Nozzle Plot
- Essentially a cone to channel larger particles
- Conversion dynode plot SI vs. Ion mass
- ETP has mass bias, esp. above 100 amu, but SEM218 doesn't
- Approaching ng m-3 detection limits but IE 10-5 may be the limit (max)

Operational Upgrades/Development

- Temperature controlled inlet, understand scaling factor
- Inlet temperature, pressure and RH measurement, fully characterize sampling conditions
- New rack system, to transport easily
- Beam width probe, understand scaling factor, need to engineer and software
- Optical particle detection, problem with background scattered light, but working prototype, get higher size resolution and properties of non-volatile particles

Plots

- Design concept for single rack mount, right or left handed
- Wire probe of beam width, 75 micron wire across heater to measure transmission, try to use routinely to determine how much is actually sampled
- Temperature controlled inlet, liquid coolant used during ITCT (UMIST), peltier cooled being tested at BC.
- Light scattering module, 532 nm with 25 mW ellipsoid mirror
- Most important improvements
  - Beam width probe and converging aperture

Hardware Failures

- Premature bearing failure of turbo pumps on the front end, inlet and back pressure too high, solution bigger pump and Alcatel hybrid pump
- Alcatel hybrid bearing problems, new release planned for Oct 2002
- National Instruments fast board data acquisition failure, solution by replacement
- Balzers components, RF QMH 410-5, IS420 recessed pins in the ionizer connector
- John: "We'll do what we gotta do!"

Hardware Failures, contd.

- V301 premature failure, infant mortality case
- Vacuum Interlock (TP6), shut down of multiplier, heater, and heater bias, V70 controller reverts to low speed operation
- Pin-hole assembly tightening, over tightening deformation of disc, low pressure side o-ring disrupts particle transmission
- 5V (not sure what he said here)

Difficulties …

- Cabling, need to explain better, some left unconnected
- AMS acquisition program, corrupt AMSmenu.prm, don't close with "X", hit the enter key!
- Balzers IS420 loss of V6 and V7, power glitch that resets SEM to FC and disables V6 and V7 (discussed in manual)
- Computer instabilities, dual vs. single CPU, works better with single CPU, but want dual to support light scattering system, working in house and trying to come up with a stable design
- User manual … troubleshooting and debugging section

Chopper Zero Issue

- Plot of ion signal vs. TOF time for various frequencies (is t=0 measured properly?)
- Systematic offset means zero isn't correct.
- Peak TOF(s) vs. 1/chopper frequency plot
- Need to carefully evaluate effect on size calibration when chopper freq is changed.
- Velocity cal. accurate for only the chopper freq that was used.

Maintenance

- Pin-hole assembly, check o-rings and replace with 2-006
- After field mission clean the chamber and filters on all systems
- Last thing? (don't know what he said here)

Questions

- Johannes: Problem with turbo controller on aircraft? Theirs failed back in the lab. Didn't restart pump, talked to Varian for an exchange and thought it might have been due to temperature differentials.
- John: temperature spec rating says it should be OK
- Keith: also had problems, overheating in Switzerland
- Jose: mounted another fan and that solved the problem, flashing light is a warning
- James: Alcatel was cutting out, even with fans working, TSI 3800 might have accentuated the problem.
- John: Only happened when two controllers stacked.
- Alice: Alcatel controller did fail during one flight, restarted the pump to solve.

Feedback for John's Presentation

- Jon: issue of nominal pin outs, problem of preamp, troubleshooting in the lab
- John: manual is evolving
- Eiko: electron multiplier aging? Clean?
- John: running in the field with m/z =28 is killing multiplier, shortens the lifetime, tested running w/o 28 in TOF list and EM didn't drop as rapidly, follow up during airplane talk
- Eiko: refurbishing?
- John: discrete dynode can be cleaned, but better off replacing
- Jose: if cleaned, might get some of the gain back
- Guenther: changes the value of the deflection plates, helps for the first while until a replacement can be done, old ceramic bodies will be discussed.
- Ann: operate with the voltage as low as you can

Guenther: Inficon/Balzers Vacuum

- Current and future improvements on Q-pole ionizer
- Part I: QMS applications and integration into analytical machines
- Part II: optimization of the Q-pole at Balzers
  - Ion source and deflection unit
- Part III: future Q-pole ionizer improvements

Inficon QMS Development

- 1962 etc.
- 1997 , QMG 422 new electrometer preamplifier and auto ranging
- 1993, Balzers and Leybold were merged
- 2000 , new name Inficon

Principle of a QMS

- Schematic diagram of operation
- Pressure in the MS < 10-5 mbar,
- Otherwise degradation of the EM lifetime
- Generalized diagrams of various ion sources, ion optics and energy filters, mass filters, and detectors, and gas inlets

Photos of different Mass Filters

- Show sizes of various mass filters
- John: why 16 mm hollow?
- Guenther: weight
- Jose: Hyperbolic surfaces?
- Guenther: as long as peak form is conserved, get better peak shape, not designed for UHV (glue), need to choose other ceramics to make bakeable, factory cleaning includes baking

Data on Mass Filters

- Big table
- Contribution to the neighboring mass He to 3 amu (10 ppb for ?)
- Mass Filter and applications
- Table of different applications for the various size filters (6 mm – 100 and 200 amu, 8 mm – 512, 1024 and 2048 amu, and 16 mm – 128 and 340 amu)
- Write the date to know what the name is

Optimization of the Q-pole

- Used in the AMS
- Cross-beam ion source
- Higher ionization efficiency with magnets or increase emission current
- Field axis technology transmission and precision of the rod system
- Discrete dynode SEM
  - Current amplification, ?, and geometric design

Higher Emission Current Plot

- Ion current vs. emission current
- Ion sources behave as individuals, can't make them 100% equal
- At 8 mA, sensitivity increases by factor of about 4-6 compared to 1 mA, need to carefully retune the ionizer as current is increased (at every new emission current)

Cross Beam Ion source plots

- Flight paths of positive ions
- Flight paths of electrons, filament injects e- into the formation chamber, highest density close to the filament
- Put together: profile of ions generated by e-, ions extracted more or less efficiently, heat sensitive volume in the ion source, point is to make the sensitivity better by matching the volumes
- Doug: oven is just behind this volume so that the vapor plume is coming out right into the ion source volume – want to maximize the ion density there
- John: Alice walked the particle beam across the ion source region, have mapped out that density crudely
- Guenther: extraction efficiency gets less as you move the vapor towards the filament
- Designed compact ion source (passed around room)

Deflection Unit

- Pair of two concentric plates non-spherical shape in the direction of the SEM from the mass filter
- Deflection inner (V6) and outer (V7) voltages
- Maybe use a 90 degree deflection unit with spherical device, causes mechanical problems
- Inline version increases signal and noise, maybe a slight angle instead?

Field Axis Voltage and Electrically Isolated Analyzers

- Electrons can impact on chamber walls and cause desorption, but with positive bias e- can only impact onto the anode well defined surface, get more reliable emission current and background is reduced
- High energy ions (170 eV) can be accelerated with high voltages to cross the fringing fields, ions have 10 eV in the mass filter after being decelerated by filter voltage bias
- peak shape is also better with the field axis technology
- Stop doing it before the peak shape looks like a bird's wing
- Doug: useable field axis voltage 10-14 V, been running too low, should be closer to 13-14 V
- Guenther: increase the field axis voltage to maintain nice peak shape
- Jose: Balzers' manuals on the AMS web page
- Manjula: also on the ftp site

Results till Oct 2002

- Increased emission factor of 4-6
- Compact ion source factor of 2
- Magnets: no improvement? Spiraling might be causing peak broadening
- John: electrons the only thing that get perturbed
- Mass Filter theoretically factor of 2
- Lower deflection voltage factor of 2
- other deflection unit maybe factor of 2-3
- Thoriated filaments

G's Questions

- Eiko: Can run 2 filaments at 2.5 mA (1.25 mA each) to get linear increase in ionization efficiency without degrading filaments as quickly?
- Guenther: two filaments at the same time changes distribution of ions in the source, but move up in space charge limits
- Jose: separate controls?
- Guenther: discuss with electronics guys about IS420, test if minor change
- Jose: effect of magnets? Bigger ionization volume?
- Guenther: increases paths of e-, higher
- Jose: time broadening?
- Guenther: distribution of ions greater in time
- Jose: so, volume bigger.
- Doug: spend time tuning the ionizer better, different tuning procedure than now, may be able to reduce the tail by playing with the ion optics
- Eiko: done with compact source?
- John: Yes, but testing with old source.

G's Questions, contd.

- Doug: both non modified IS420 and old ionizer in the field, procedures and cost of upgrading? Have another? Worthwhile to clean.
- Guenther: replacement of the ion source, need to look into how expensive, makes sense if the users change the ion source, refurbish with the filaments, thing with EM also makes sense not to throw away the ceramics.
- John: ionizer cleaning procedure?
- Guenther: simple, take apart lenses and clean with scotch bright or sand with plastic paper with small grit and supersonic baths. Abrasive cleaning followed by chemicals (trichloroethylene in old days). Ethanol and PA in supersonic bath with 100 C.
- Jose: heater can go to 1200 C, heat up overnight decreases the background
- Guenther: Discuss with Unexus (split) possibility to include such devices into the vacuum chamber.
- Jose: already have it
- Guenther: might not already be done for ions, can get rid of the junk but it has to go somewhere.
- Doug: shooting low volatility material directly into the ionizer, walls of the ionizer become outgassing source, so heating the oven to 1200 C can be effective because it heats the ionizer and walls.
- Guenther: but ion source sensitivity could also be changed, so need to develop UHV procedures

G's Questions, contd.

- John: Degassing procedure? Is 10-6 or 10-7 Torr too high?
- Guenther: slightly increase emission current to degas, but don't switch degas on, do for about 15-20 minutes.
- John: emission current or voltage change?
- Guenther: both
- Jose: baking with filaments off?
- Guenther: baking with filaments on, filaments are last to switch off, measurements with thermocouples lasts about 1 hour because heat loss is slow, not so much radiation, suggest filament current on first, then bake, heater off, then filament off.
- Jose: cleaning summary? Remove ion source to see if additional cleaning will help.
- Doug: My experience – first time with Balzers, most reliable and robust, simplest, believe key to this besides quad, ionizer, focusing ions, fraction of ions formed is larger and this is key to the high sensitivity, system is incredibly stable over days, better than he expected.
- Jose: support? RF failed in field, replaced with already existing replacement. If not available, what could be done? Tried to return unit to Balzers, but not end user, given the "run around", need to set up some system so that a replacement could be sent quickly,
- Guenther: job for me and Steve to talk about, we'll find a way

Open Discussion

- S-M Li: cleaning?
- John: under vacuum with heater and filaments on, see increase in background during sampling, but goes down, "self-cleaning". Explore degassing operation to help speed up process
- S-M Li: benchmark for background value?
- John: keep it pumping, monitor background in program with "check status" convenient way to check background levels
- Jose: compile series of benchmarks, talk about later
- Manjula: other failures?
- Keith: transportation? Rods loose the top end, tighten OK or does the position need to be fixed critically.
- John: rods aren't changing because on ceramic holders, deflection plates should take care of it.
- Keith: need to design a support to take care of it
- Hugh: shipping quad separate from instrument, baffle holding it into chamber, need shipping collar.
- Jose: never take quad off
- John: ship units all assembled, just plug it in
- Keith: ship John in it as well

Manual

- Tool for teaching new users
- Repository for combined knowledge of users group
- Hopefully, looked at the manual

Structure?

- Operating procedures (hardware)
- Software
- General comments
- Ann: add printouts of all menus
- Frank: details vs. basic summary
- John: too much detail, overwhelming
- Frank: quick start guide
- Manjula: format to separate it
- Manjula: missing parts?
- Jon: shipping the instrument
- Ann: standby mode section
- Hacene: right after delivery
- Manjula: John has one
- James: emergency shut-down procedure
- Jose: close inlet
- John: switch off all valves

Manual Discussion

- Erik: check sheet?
- John: Jose's got that
- Manjula: MacDonald's sheet, very detailed version
- Alice: disagreement about timing of procedures, hard to generalize, maybe one for each application
- Jose: working on that, nice to have structure, great tool for teaching people
- Manjula: integrate some version of that
- Ann: initial procedures jumped around, venting last, also names of procedures need to be the same as in cal section
- Erik: non quantified statements, e.g. not pumping down fully, signal low
- John: didn't give quantifiable, user should make note of the settings
- Jon: write for expert and put in front of it a section for the new user
- Jose: troubleshooting section
- John: recommends table format, started that
- Jose: should circulate that

Manual Discussion, contd.

- Frank: addresses and phone numbers of various support, including suppliers
- Alice: technical information has list of companies, part, outdated price, and phone number
- Johannes: depends on where the campaign takes place
- Manjula: Anything else missing?
- John: chopper zero, later on in manual
- Manjula: quick start, gory details
- Jose: summary
- Eiko; different version of instruments
- John: older instruments shouldn't be included
- Keith: for teaching
- John: clunky
- Alice: have old instrument, tried to put in numbers, but don't have them
- John: archive manual for older instrument
- Jon: upgrades make several
- Alice: reference different sections or versions of manual
- Jon: beginning of manual say which version that it covers

Manual Discussion, contd.

- Hugh: tables of figures of merit depending on each version of the instrument, put in method and referred number for particular instrument
- Eiko: calibration sheet for reference
- Hugh: helps to determine qualitative changes
- Alice: John ships a sheet for the instrument when it is shipped
- Manjula: pump powers from Jose's sheet as a function of time, use it in the field, plus power point screen captures
- Eiko: problem for new people trying to determine baseline, default on the ion gauge?
- John: don't ship it any more, nobody else needs to know that
- S-M Li: model numbers?
- John: keep track of what each instrument has by serial number when shipped out the door
- Jose: table at the end
- John: don't want it to be so big
- Jose: website has everyone's info
- Hugh: that is extra information
- Manjula: need to do better job separating

AMS Data Acquisition Program

- Distribution of recent versions via ftp read-only site
- Find newest version according to version numbers (current is 3.2), no broadcast when new version is uploaded
- Incoming site is password protected
- Alice: email comments
- Eiko: correction factors is very brief, say what fragment that is based on
- Doug: that will be discussed tomorrow, updated

Software Changes since last year

- Using LapLink (Harvard Forest during the summer), also there are other programs that do the same thing
- Hugh: LapLink does not work thru firewall, need a tunnel thru firewall
- Eiko: also used VNC

Modifications of Parameter Menu

- Goal: Simplify, separate high frequency changes from low
- v. 3.5.8 latest
- Default contains parameters that shouldn't be changed often, factory set, but check!
- Example: hardware information TOF distance, quad in use, chopper duty cycle
- Data Acquisition/Saving: make sure that the new board is set to the correct device numbers
- Software: no one should play around with this, esp. w/o data acquisition and simulate chopper signal
- James: all sorts of problems because simulate chopper signal is sometimes yes if EM cal is stopped before finished
- Manjula: if that happens it should appear in the status log in the main menu, need to figure out the most important errors and reduce the log size, try to focus on just warnings
- AMS operating mode: discussed later

Regular Parameter Menu

- NOT Crashing program is getting better
- Analog input channels is now being saved with each itx file, use them!
- Should be able to read volts as well as conversion using calibration in the panel
- Desired voltage range, used to say desired gain, plus/minus implied and she will put it in (new)
- Jon: saving?
- Manjula: auto save interval of slow boards for faster saving
- Averaging and Saving: needless ones removed, efficient data saving mode not yet implemented, soon moving toward HDF
- Data Acquisition Boards: varying rate, noise with high frequency can be reduced using fast acquisition rate, but less masses can be studied because of buffer size
- E.g.. 1 MHz (40 masses) with 4 MHz (only 17)
- John: put max # masses in
- Johannes: Windows 2000 instead of 98
- Ann: stay with 2000?
- Manjula: yes
- John: if the computer is stable, don't change it
- Manjula: page lock error
- Doug: extremely important to make those numbers (sampling rate) as large as possible, S/N and ion background reduced, works at 4-5 MHz, but can crash intermittently if too fast on slower computers

Parameter Menu

- Multiplier and chopper tab: put negative numbers in front of servo values to do manually (used to be 110-180)
- Mass Spec tab: Johannes unreasonable values set in mass calibration intercept and slope
- Rest is pretty normal, nothing new, unless someone sees something
- Flow calibration also same
- Single Particles: light scattering operating but should be off, not supported for everyone
- Parameter Menu converts Version 2 to Version 3 (less than 3.8.3 cannot read the new menu). Log files records date saved (menu.prm)

Mass Spec Window Display

- Goals: help interpret signals
- Mass value box rough reference of loadings, but doesn't include scaling factors, fragmentation, isotopes, etc.
- Integrate isotopes into mass loadings same as James' program by reading fragmentation batch files, also have detection limits listed

Calibrations

- Simplify
- Nitrate IE, Calculate IPP from region 2 only, can also do ammonium, individual fragments as well as species
- Quad mass/resolution calibration: automated user friendly procedure (don't have to type as fast as Eiko did), won't be crashing out
- stick intensity calibration done automatically around m/z 28, works in every case except where signal is high (was 18 last summer)
- Eiko: 28?
- Manjula: in the mass spec, will add choice for air beam mass
- Way it works: maximize broadening but stop when it starts to leak into the previous mass
- Jose: no one has the new software, set the width to 1 amu, broader will cause TOF to not agree
- Manjula: everyone should be able to upgrade except eddy correlation acquisition
- Manjula: new changes in the next week and then release 4.0 in the all uses directory of ftp site

AMS Operating Modes

- Most users should not be playing around with them
- Eddy correlation: synch TOF with 10 Hz anemometer works for only 1 TOF mass
- Airplane: Caltech twin otter
- NYC Alternate Mode: 2 s MS/TOF does it all in “one go” still buggy, only used by us for RT measurements behind busses. 0.3 s data for individual mass and 4 s data for entire spectrum
- Johannes: use for aircraft data?
- John: TOF masses limited to 6, and mass spec is not toggle
- Manjula: actually had zeros for 28
- John: 30 s
- Jose: down to 20 s, make (?) numbers very small
- Doug: latest versions of James’ program can’t deal with data faster than 30 s

Light Scattering Mode

- Doug: “By George, we’ve got it!”
- John: better size resolution, smaller peak width
- Doug: see particle from laser, earlier than TOF data because different timing

Saving Data

- HDF: binary format, 5 groups (TOF, MS, Run, Mode, SP), saved as matrices
- Control via Digital Signals: saves on every change of digital state of specified line, data averaged after specified delay
- John: saves on low to high, high to low transition?
- Manjula: yes
- Hugh: Jungfraujoch – external trigger for switching inlet, one save lasted about 12 hours, lost best cloud, need an override if longer than a fixed period (valve got stuck)

Future Updates

- Continue simplification
- Computer controlled ramping of oven temperature
- Jump MS mode: scan selected masses
- Saving in HDF
- Setting menu parameters via files/macro language
- Integrated mode for switching between the various operating modes to mix and match
- Doug: should become default mode using Jump because increases S/N
- Eiko: override other modes

Questions:

- Software changes with bigger user base?
- Open source? - NO!
- Separate programs that interact with AMS, e.g. temperature controlled inlet, switching between valves in Prophet, moveable wire
- Specialized modules integrated: NYC alternate, eddy correlation

Comments

- S-M Li: online help menu?
- Manjula: supposed to be able to get to the various ftp and websites, put part 2 of the manual into the code
- Eiko: make it into a html
- Jose: links in PDF
- Jon: not hard code file locations?
- Manjula: possible to add that in, maybe use two menus

James: Analysis Software

- Show current version with trial dataset
- Lot of improvements with deluxe version 1.2.5
- Biggest single improvement by handling data in matrices
- Ask questions as we go along
- John: -9999 should say testing magnets?
- James: first save that it loads

Loaded Data from Lab

- Doug: select run interval for air beam at the bottom of the list
- James: easy
- Split up corrections:
- John: type in reference numbers or cursor?
- Do either.
- One point of the air beam, use only that one. Ideally use only one calibration, but need to determine good way of doing that.
- Won't spend ages doing corrections it's already done.
- Recalculate sticks: m/z calibration drift and handles open/closed MS differently reduces artifacts
- Error Parameters: same as before
- Doug: Units for background?
- James: Ions counted per square root seconds, I don't use it
- Doug: put it there
- James: artifacts in logging software, calculates baseline from that

Using Deluxe for Lab Data contd.

- TOF corrections: clean TOF signals – removes last few points too high or low
- Overwrite DC markers: checks all the m/zs and recalculates TOF traces
- Ann: recalculating Da for whole dataset?
- James: velocity cal changes w/ f(pressure) ultimately apply to software, but not in there yet
- Ann: IE corrections applied to all data
- James: yes
- Doug: this is all James' program for correction should do, should be up to the individual user to fix
- James: waste of my time to include all kinds of processing, everyone should do their own
- Jose: write your own program and execute it on top of James' program
- James: open source code, appreciate any feedback, give acknowledgement if used for paper
- Paper for JGR accepted that contains the majority of the underlying math in addition to Jose's paper, good place to start from
- Talk to me directly about the nuts and bolts

Examples

- Eiko: mark range of runs to apply correction to?
- Correction wave: AB measured with MS mode , no idea what's going on (peaks in Correction Factor)
- Instruments response to the AB should scale linearly with AB, change in sensitivity of particle phase should be scaled with AB
- Every time a EM cal is performed, ideally should see AB go down with time and then back up after EM cal, in practice it doesn't always work for a bunch of reasons. Analysis code just scales the AB.
- Doug: wave defined to scale all the masses
- Jose: see sharp jumps like this, mass cal of quad is shifting, James' program is able to deal with that.
- Wave called CorrFac contains all this info

MS Averaging Tab

- Use same batch files to calculate mass loading from Hz
- Whenever a mass is calculated the cal factors are applied.
- Eiko: Ammonium applied from 0.44? How is it done?
- Doug: talk about this tomorrow
- Johannes: wrong mass scale, how to correct it using James' program
- James: can handle changes to slope or off by more than two m/z, never had that problem before, should be relatively easy to stick in
- Generates legend with mass loadings for each species (scaled, but average MS shown with nitrate equivalent)
- Can also display signal in logging software (choose "all" for data to average), open and background raw data
- Doug: rephrase that: anomalies in the data that don't make sense by showing how the sticks were calculated from the raw data
- John: colorize
- James: put in list
- Jose: look at waveforms, if TOF doesn't look like size distribution it's wrong, especially in the limit of low signals

MS Time Series Tab

- Simple time trends can also do simple math: e.g. 48+64/etc.
- Mass calculations: works the same as it always has
- Code shows axis labels as constants in the code (change mass concentration to Japanese, German, etc. in one place for all the graphs) – under "Axis Labels" in code

Load Data tab

- Eiko: load, discard, update, List?
- James: load: new, all, or specific runs
- Discard: deletes specified runs from memory
- Update: checks each one and deletes or reloads as appropriate
- List: just makes a table of the run times and numbers

TOF Traces Tab

- Problem loading TOF traces because 28, 32 need to be in TOF masses, unclick scale to TOF air beam
- Hasn't changed much over the past year or so
- Data to plot: 4 choices
- Smoothing, normalize to MS
- Johannes: normalize vs. scale to MS air beam? Scaling to both ABs?
- James: TOF AB as f(TOF AB) vs. MS AB, departure causes TOF data to be different
- Doug: Normalize to MS always applied, neither one of the scaling buttons mean anything to us so remove, and make it clearer how these are connected
- Johannes: scaling to AB?
- Jose: recovered changes by looking at AB in TOF mode

TOF Image Plots

- Johannes: default settings?
- Not really, varies campaign to campaign
- # SDs 1 or 2
- Spike in the data causes strange automatic scaling, do manually
- # SDs to ignore below: anything below is interpreted as noise, straight line as f(TOF) and then overlays white there in image plot, negative values below SD value, offset is big black spot
- John: classic picture of lab air, airplane use struggled, Da max was too large, automatically determined?
- James: put in default values, depending on velocity cal it can get confused, will put in safety net
- Eiko:? (don't know what he asked here)
- James: Improve that, integration between minimum and maximum diameter, stick something onto the panel about that

Misc. Tab

- Remap Time Series: Use to compare with other time series on different time basis
- Custom Colors: table needs names to color traces to apply specific colors, in order of priority, only match part of the name
- Doug – list for James: 1) view list, make that view color list
- 2) Make default thick and then "thin" the control button
- 3) add zero line to TOF plots
- Options: time and smoothing are obvious
- Save Batch button – for fragmentation, batch, and color waves, one more to put on would contain comments to make library for each campaign
- Johannes: load batch?
- Doug/Jose: load by clicking on itx file
- Doug: have to become familiar with Igor!
- New bits: selectively average runs in the MS average and TOF average by some other criteria, wave of 1s and 0s, mechanism is there to write external macro to create wave, not been tested yet
- Batch list and fragmentation list with time-dependency in waves, occasionally fragmentation ratio is within certain peaks, put in math for that but not tested yet

Discussion

- Jose: link to website to get newest version, make list of people's versions?
- James: stop using old versions, few buggy versions floating around, use unified version if can't get this one to work
- Eiko: correct data as often as calibrated?
- James: problem is that it's complicated, not apparent correct method to do that, need to look at each data set individually, use another program to generate correct calibration wave
- John: supply wave for user to put in CorrFac wave (default =1) separate from program's CorrFac wave.
- Eiko: HDF data?
- James: not usually need to put that in
- Jose: Don't touch James' program, need to keep track of changes, do all programming in default procedure, email Jose if you have general program that others can use.
- James: Write in C and plug in
- Jon: spike of zero in TOF data by taking lowest quartile as zero
- James: apply to the end of the TOF signal, haven't done anything to the beginning
- Jon: spikes in the beginning of the signal
- Jose: noise in the chopper speed is causing some of this problem
- James: might be worth sticking in

Additional Discussion

- Ann: A/d channels input read into program
- James: now in the load data tab
- Doug: read and generate waves from A/D channels in the itx files,
- James: that's what it does.
- Doug: names for A/D channels in data acquisition use to create wave names
- James: Feedback appreciated! Can add extra bits, read me at the top of the file.
- Manjula: thank James, and acknowledge in the paper
- Hugh: reference JGR paper, please bear in mind that James is starting his final year of his PhD
- Manjula: Tutorials from Wavemetrics, Balzers
- Guenther: short discussion of introduction for user of this instrument, Licht – 1 week course, 1-2 day course here
- Manjula: Link for next year's AMS meeting
- Guenther: special questions before we make the course
- Jose: email list

Jose: Figures of Merit

- Parameters to keep track of:
- Particle transmission efficiency, 100% relative to CPC at 350 nm
- Sensitivity: detection limit =3*sigma of 1-min data when there is a filter on the inlet, benchmark for NO3 ~ 5 ng m-3 (G-1 instrument), same as signal to noise ratio
- Doug: compare to prediction
- S-M Li: filter?
- Jose: any kind of filter
- Signal Intensity: IPP for m/z 30 +46 when sampling 350 nm (mobility diameter) pure dry NH4NO3 particles, calibrated DMA with PSLs, Duke PSLs can be off by 4% in Dp or 15% by mass, maybe use NIST PSL size standards instead.

More Measures of Signal Intensity

- Ionization Efficiency: ions detected per molecule evaporated, same as IPP, more meaningful units, determined by mass calibration, oldest 2e-7 ions/molecule, newest 8e-6 (1e-5), related to amps per Torr not used any longer because it is not fully determined
- Air Beam Signal: depends on instrument configuration, newest 1.4 e7 Hz for m/z 28 (John thinks it's saturated), oldest 1.0 e6 Hz for m/z 28. Subtle things can go wrong and screw up calibration: Crystal Face 30% change in AB due to orifice problem. Use 32 if 28 is saturated.

More measures of Signal Intensity

- Ionization efficiency to Air Beam ratio, should be constant and change with ionizer tuning, newest 8.0 e-6/1.4e7 = 0.57 e-12 = 0.57 pAB (pico Air Beams)
- Doug: roughly within a factor of 2 of that, AB is a pretty good indicator of the ionizer sensitivity
- Jose: spatial distribution of AB molecules is similar.
- Show Worsnop-Jayne's Law: detection limit of NO3 vs. time, 5 x sensitivity per year

W-J Law Part II

- X3 signal every year looking at IPP nitrate vs. time
- Other plot?

AMS single particle detection

- Increasing particle TOF/Da, sample TOF trace as f(time)
- Background ion noise at some frequency, sensitivity m/z dependent, makes it harder to distinguish ions from particles, electronic noise ~100 kHz? Power line, switching instrumentation

Electronic Noise

- Dominant for high masses
- Affects sensitivity, if noise large need higher threshold
- Example: in MS mode, switch off filament and multiplier, look at third RMS number 11.5 with filament off, 3 with multiplier off, relative to noise, with Crystal Face instrument changed from 0.5 to 2 every day, if 10 or constant there is a problem with electronic noise.
- John: toggle mode?
- Jose: little peak of potassium showing up in MS
- James: multiplier vs. filament off
- Jose: can get some surface ionization if filament not off first.
- Example: TOF mode, look at MS: \Rel 6 (kind of high)
- John: any masses in TOF mode?
- Jose: yes, they should all be the same unless some noise is coming from the quad
- Doug: there will be an easier way to do this with the new EM mode
- Jose: a lot of noise
- Doug: one number to look at, threshold number for a mass w/o background should be about 0.4 bits, figure out why if higher
- Jose: many other parameters that are related and agree how to talk about noise

Ionizer Tuning on Screen

- Walk the voltages and look at the signal
- John: do on 32 because 28 is saturated
- Doug: the most important thing during tuning routine look at curve, there should be a peak, no peak is indication that something is wrong, this one is tuning as well as I've seen, size of peak varies, once pumped down for fraction of a week, this stays stable and shouldn't be checked unless AB changes dramatically
- John: should check but don't accept changes
- Doug: in practice haven't been able to go back to old signal with old values
- Doug: cancel doesn't do anything except close window!
- Jose: need to input old values in Balzers menu (look at tuning log for old values)
- John: was a big change for heater bias
- Jose: biggest influence on signal is heater bias
- Eiko: not seeing a clear peak
- John: you need to talk to me
- Jose: extraction voltage is the only thing that is flat
- Doug: deflection voltages with new IS420 module, tunes with finer resolution, it's worth upgrading
- Ann: how?
- John: Work up a plan.
- Jose: pay attention to range of voltages, too, should be somewhat parabolic

EM cal on screen

- Switch off ionizer and determine threshold above background ions
- James: first point on the curve as the voltage is ramped looks strange
- Jose: some software thing, don't pay attention to it
- John: sinusoidal curve on the bottom plot is characteristic of the ETP multiplier and ?
- Benchmark: Gain between 2 and 4 million. Do alt-print screen and copy into PowerPoint to determine problems faster.

Doug: AMS Detection Process

- Key concept of three processes
- 1) getting particles into ionizer
- 2) vaporizing once they hit oven
- 3) ionizing the vapor plume
- All the ion signals we can detect are quantitative. Measure Ionization efficiency. Need to know fraction vaporized, and fraction are getting to oven. Need to improve ability to independently look at those three processes.

Sensitivity

- Ionization efficiency – nitrate equivalent mass
- Vaporization – volatility vs. heater temperature (refractory ~ black carbon + crustal oxide). Can detect sea salt with high enough temperature!
- Particle transmission and collection, lens focusing, aspherical particles

Jose: Coming Back to Background (Ion) Noise

- Dominant for m/z 30, 44, 46, 48
- Reason why DL is high for these species instead of organics (?).
- Look at check AB graph? Relative background graph much cleaner at 30 than 184. Lib Peaks, background up when heater on, but should go down over time. Useful to have for your instrument to monitor changes.

Jose: AMS calibration Math I

- Look in James' paper or Atlanta paper for details and equations
- 1) Ion flux correction for quad transmission and multiplier response (haven't been doing systematically)
- 2) Molecular flux vs. ion signal
- 3) species mass concentration

AMS calibration Math II

- 4) Empirical relationship between relative IE of different species. Nitrate equivalent mass. IE for species is linear as f(MW). Show graph: Electron impact ionization cross section vs. number of electrons in molecule, slope of line is IE vs. MW, Phil has done quite a bit of work determine this.
- 5) final expression to calculate species mass concentration

AMS post calibration

- Evaporated flux
- Changes to correction factor due to particles not focused due to shape, size cut of lens, critical orifice, slow vaporization of low volatility species
- Cs scaled = Remp* Cs
- Report results as non-refractory species (e.g. NR sulfate)
- Doug: get relative response which is a scaling factor and want to go beyond empirical value.

Doug: EI Ionization cross sections

- Ultimately separate that calibration factor into two components
- Compared to other MS systems, particularly GS/MS, is that we are adding up all the ions, they use calibrated specific ions
- We know the gain of the multiplier and add up all the fragments to get total signal or absolute mass loading.

Gas Phase Ionization Cross Sections

- Phil Silva's data:
- Relative ionization cross sections vs. Mass
- Nitrate equivalent cross sections vs. mass
- - nitrate/organic = 0.7
  - Blue line normalized to 1, nitrate is lower because not counting all the fragments
- Clearly do more work to extend calibration to more species, but this seems to work, basis for relative calibration factors
- Particle collection efficiency taken out, but the range of error bars is an indication of that.
- Everything we're doing is essentially based on this curve.

Aerodynamic Lens Focusing

- Plots from John's paper:
- Streamlines and collection efficiency
- Since then, managed to manufacture transmission efficiency plot using field data.
- Zhang et al. lens transmission curves, including "Best" lens that has never been made, have impact limit of 40-45% on first lens, particle bounce in lens and some fraction is still transmitted, no good way of generating particles

Small Particle Transmission Curve

- Transmission vs. Da
- Smaller critical orifice to limit flow rate
- Show Edinburgh and Manchester data, two different lenses?
- NYC data low end cutoff due to transmission, high end could be due to transmission
- Other studies (NYC plume chasing), not necessarily actual size, but transmission cutoff

Pinhole vs. Converging Orifices

- Streamlines diverging more for pinhole than for converging orifice, especially for 2 micron particles
- Demonstrated in a crude way by sampling an asthma inhaler
- Drug particles larger than carrier gas particles, transmitted better thru glass "converging" orifice than thru pinhole
- Still work in progress

Plotting Particle collection efficiency

- Walk beam across the heater by tilting beam
- AMS collection efficiency as f(beam position)
- Nitrate detection efficiency is also flat
- On one side of the oven the efficiency increases because it's on the filament side. Improved by using the small ionizer.
- Overall collection efficiency is actually now very sharp, define edge of oven really sharply, therefore beam is very well-focused.
- Ammonium nitrate particles well-focused.
- Ammonium sulfate is not as well-focused. Beam is wider than the oven, and ions per particle is the same even when hitting the edge of the particle beam.
- Still need a scaling factor on the order of 1.5 to 2.
- Eiko: why is it 2? Transmission is 15% for sulfate particles, but close to 70% for nitrate.
- S-M Li: ?
- Doug: Particles in the field are more spherical. See the same thing in the field for various studies, scaling factor is fairly constant. Need to implement beam width on ambient particles in the field.

Particle Collection Discussion

- Phil: organics showed similarities to sulfate. Ambient organic to OC?
- Manjula: Houston, within 10%
- Doug: extra scaling factor of 1.5 to 2 associated with poor focusing of ambient particles.
- Ann: Using delta pattern to refine factor for calculating organic mass from OC measurements with Tim Bates on ship.
- Hugh: organic is size dependent, need to look at that quite carefully.
- Jose: mode dependent? Need to be investigated in more detail
- Hugh: nitrate data matches, not internally mixed with sulfate
- Richard: Why?
- Hugh: acidic sulfate, young fresh emissions, nitrate forced out
- Jose: nitrate in sodium nitrate mode, also calcium nitrate focusing differently

Summary

- Small particles down to 30-40 nm
- Large particles up to 700 nm
- Open question for larger particles, need converging orifice
- Aspherical particles - need moveable wire and better generation and characterization of larger particles
- Jose: APS is not a black box,
- Ann: measure particles optically in front of the lens?
- Alice: Darin's working on that
- James: use VOAG to generate particles
- Jose: AMS was the only diagnostic that VOAG had a problem, works poorly at 1-2 microns, OK above that
- James: worked OK for him at 1 microns
- Hugh: small sizes match to measured distribution, non-spherical particles with non-uniform density, effective density of 3, no particles below 90-95 nm.
- Jose: depends on aerodynamic diameter
- Hugh: wrapped up in effective density, haven't gotten to the bottom of it, but that's what we see

Vaporization

- Optimal temperature?
- Heater temp vs. heater power – everyone should generate with the new instruments,
- Three axes, heater current, heater voltage, and temperature

Plot for Heater Temps

- IE vs. heater temp
- IE/AB vs. heater temp
- Sometimes at higher temperature these drop off, parabolic shape

IPP vs. Heater Temp

- Dioctyl Sulfate (DOS), also has a peak in the IPP around 550 C.
- Believe in the field it isn't as sharp, but it is true that more fragmentation occurs at higher temperature.
- Jose: ? (don't know what he asked here)
- Doug: That could be part of it, but it doesn't explain all of it.

Heater Experiments

- 550 C is a special temperature
- Different results from Frank for ammonium nitrate, sodium nitrate, and potassium nitrate, looking at the width of the particle signal in TOF space.
- See those plateaus by looking at the single particle pulse width (< ~150 ms vaporizing all of the particle).
- Also see in the counting efficiency approaching 100% at the same temperature.
- Copper sulfate, ammonium sulfate.
- These curves are why we chose 550 C, minimize fragmentation of organics and maximize inorganic vaporization
- Contradiction with some other results.
- Tim: sulfuric acid?
- Doug: vaporization is even easier with sulfuric acid, make ammonia, sulfuric acid, SO3 and water.
- Should see some sodium nitrate
- Ann: did see sodium nitrate at that temperature, but need to check how quantitative.

FP_0801_1 & 2 Study

- Remnants of propellant when cannon shot off
- Labeled as sulfate and organic in the spectrum, seeing zinc (m/z 64, 66, and 68) in the spectrum
- Point is that we were able to change the oven temperature in a minute or so
- Mass spectra at the two temperatures, fragmentation pattern changes
- Organic signal largely disappeared.
- Problem with cycling because background is changing with time. So background subtraction doesn't work. Very clear that the physics of the vaporization process if the oven temperature is varied we see different things. If we don't vary the oven temperature, we are never going to see refractory components in the atmosphere.

Frank: Mass Concentration

- How to calculate?
- Use several correction factors for:
- omitted masses (fractionation patterns)
- IE differences (IE measurements)
- Sampling Losses (?)

Fractionation Patterns

- Experiment Scheme
- Results: ammonium nitrate and sulfate
- Ammonium masses 1, 2, 15, 16, and 17 nice pie chart with relative intensity, relative error
- Nitrate masses 14, 16, 17, 18, 23, 28, etc.
- Sulfate masses even more fragments
- Biggest unmeasured fragment is 18 for H2O from sulfate
- Correction factors: ammonium = 1.05* (16+17)
- Nitrate = 1.09* (30+46)
- Sulfate 1.77*(?)

Ionization Efficiency

- Nitrate: defined as 1
- Others ?
- Organics = 0.7, first correct for all fractions and isotopes for other species

Collection Efficiency

- Compare to PILS nitrate in PMTACS-NT 2001 = 2.34
- Nitrate internally mixed with sulfate, therefore = 2.34
- Ammonium also internally mixed, therefore = 2.34
- Organics no useful comparison done yet, correction factor is unknown, measuring beam divergence or lens with better transmission to heater
- James: Paul Ziemann
- Doug: Paul has never done calibration
- Ann: Jim Smith CIMS with ion trap, done for organics and sulfate, maybe compare

Average Mass Concentration

- The “rest” in the pie chart is about 36%
- Large particles, low inlet transmission
- Maybe water
- Sulfate, nitrate, ammonium already accounted for large particles by comparison with PILS
- Thomas: cutoff with PILS?
- Frank: most of it is accounted for
- Eiko: was TEOM corrected for nitrate loss?
- Frank: should have been corrected
- S-M Li: sulfate may not have been totally accounted, maybe sulfate losses on the high side
- Frank: correction factor of 2.34 check as f(size)
- Refractory? Only 5% was EC, and 5% metals, crustals
- Water? Water lost in vacuum, but TEOM also dries particles

To-Do List

- To get mass closure:
- Good relative IE measurements
- Collection efficiency
- Lens that transmits 100%
- Need to know transmission function to correct for particles not transmitted.
- Jose: step function at 2.5
- Doug: sulfate filters were 20% higher
- Thomas: water 24%?
- Doug: can tell from fragmentation pattern in the sulfate, getting water, hard to make pure sulfuric acid (Jay Slowick), 81 jumps up, water signal just happens to give you mass balance
- Ann: 18 as f(RH)?
- Doug: seen sulfuric acid losing somewhat half of the water, compare to the phase diagram that we see, still working on that.
- Ann: suggest looking at time periods when discrepancy is high vs. low.
- Relative ionization efficiency for ammonia is 4x larger for the small quad. Basing ammonia concentrations on mass 16.

Jose: Airplane (Monday morning)

- Issues
- Pumping
- Inlet pressure, temperature
- Other issues, rack system, power supply

Background Testing

- Plot of signal as f(time)
- Two time decays (3hrs, several days)
- At one point, shut off turbos and kept pumping with backing pump
- Waited 10 minutes before starting MS
- Same pressure as venting with He
- He for 3 hours, still high background
- Baking made the background worse
- Maybe better with new systems, need to be tested
- In clean areas like Crystal Face can't afford to lose signal due to high background
- Doug: change to sensitivity calculation, advantage need to know IE and AB, good EM cal (ng m-3 in 1 min), keep the system clean (pumping), gate valve on the detector pump, don't have UHV vacuum, no gate valves everywhere, but one would help us

John: Aircraft Instrument

- Inlet system double diffuser cone with anodized piece (Brechtel) actively flow controlled with MFC
- Cabin had room to stand, AMS in the forward cabin
- Vacuum startup procedure: day and evening flights, 3-4 hrs pumping time before start up
- heater turned on as soon as P5 and P6 up to speed (vacuum interlock), set to nominal power, maybe cook it initially at higher temp
- Progressively step up with ionizer to 2.5 mA
- Trained someone to start up instrument, run it

IE/AB vs. time

- Multiplier voltage was very stable, m/z 28 was not in F6 TOF list
- Constant ratio of IE/AB = 0.75 pAB
- Systematic trend of relative gain factor preflight and post flight, always lower post flight, decays slight, interpolation, end of day flights enough time to ammonium nitrate calibration and used those numbers for the flight.
- Doug: notice the threshold, flaw in EM calculation is the threshold
- John: operate in the manual mode
- Doug: note the number because get different values depending on exactly how the threshold was set
- John: this represents an average
- Jose: more stable, reason for keeping the pumping, multiplier more stable as it's pumped over time
- John: AB complicated, unless I did single ion, we would never know

John: G-1 Operation

- End of flight isolated whole system, noted Baratron pressure gauge always less than 2 Torr, leak rate of less than a few Torr per day
- Keep it isolated!
- Corollary of background signal (m/z 55) f(time), beam closed case, ion signals measured after the first few hours, saw decay with time, in 1.5 hrs dropped about factor of 3, after takeoff, background increased due to increase in cabin temperature, was this seen when always pumped?
- MS Diff is still useable signal
- Outgassing? Yes, heat entire chamber, tried heating entire chamber with heating tapes, but that didn't work unless heat evenly
- Restek coated chamber, should reduce organic and water absorption, still saw outgassing.
- With AMS program running, ran James' on the same computer, macro to push load button, another button to add tags, computer system ultimately was stable, first computer problematic and was replaced, autoloader was useful

Summary

- Hot National Instruments Board may be the weak link (45 C max)
- General cabin temp an issue, forced air flow coaxial along sample line helped, but did not solve. Try to maintain constant temperature, could be harder in fixed cabin pressure.
- James' program on top of AMS.exe worked
- Startup/pumping procedure
- Background governed by cabin temperature, not vacuum condition
- Leak free system
- M/z 28 not scanned increases multiplier life
- Measured inlet pressure, still need to account for changes in flow rate.
- Usually got hot inside while cold outside

Discussion

- Jose: changes seen when heater turned on in the aircraft, draw as much flow as possible, sheath flow
- John: TC on inlet line and sample stream, downstream always warmer than the delivery line, despite cooling, huge thermal mass of instrument
- Jose: missing volatiles
- Hugh: Swiss see same thing in size distributions, ran ethylene glycol to maintain constant temperature

Igor: Gizmo 3-D

- Plotted sulfate as f(altitude, longitude, latitude)
- 15 s MS, 15 s TOF
- Image plot, July 22 sulfate plume above, air mass came from Ohio river valley
- Systematic testing of Restek
- Hot first to degas, then cool, more important to keep temperature constant
- Doug: most important to keep it clean, get room up to 35 C over the weekend
- Jose: constrained flow, little ventilation
- John: frame had to be enclosed with Plexiglas sides, forced air to flow thru system, took off toward the end, heat the AMS dissipated was supposed to go outside, but it didn't work.
- AMS on G-1 not the biggest draw of power, 2.6 Amps 600 W 220 V, other big pumps on the system.
- Airplane 28 V was very clean on Twin Otter, but problem with AC of plane made from DC on plane, different from ground, changed heater bias when switched over, implemented auto tuning every 10 minutes, put everything on AC, ground was well-defined.
- Balzers DC power supply

Airplane Discussion

- Took the AC/DC supplies, used Balzers box to get +24 V, took 20 Amp supply out and it saved space and conserved power, worked fine. Most of the power load went to the heater, chopper and servo took very little.
- Airplane supply of 28 V? Could be more efficient.
- Asked to run on 220 V because everyone else using 110. New systems are universal can plug into up to 240 V. Earlier version has a switch.
- Doug: G-1 everything went through one UPS, different power supplies can cause trouble
- John: better to keep on one circuit, single AC plug
- Jose: APC works well
- John: model 1400, 220 V
- Doug: bought 240 V (European), rated between 150, 260 V
- John's UPS weight 50-60 lbs, Jose's 70 lbs.
- Entire package John's 500 lbs, Jose's 410.
- John only person taking data during takeoff and landing, UPS registered switch from ground to aircraft power
- Watch DC, generators failed 5 minutes before landing, UPS covered it until on the ground, definitely want UPS.
- Jose: switching power was very clean on Twin Otter, instrument never detected anything, airplane dependent
- John: dragged power cords to the plane, other places maybe can't do that, consider bigger UPS, fueled up with the plane plugged in!
- Hugh: UMIST guys struggling with these details, pilot watched them put it in (quality of the work), no formal procedure to approve instrument
- Jose: allowed me to keep power on the plane, daisy chained, up to 1.5 hrs with the valve closed, pain in the neck to do it.

Jose: Inlet Pressure Effects

- As P changes, flow changes, size cal changes, AB changes, transmission vs. size (+ shape) changes
- Keep pressure constant, run at 160 Torr instead of 760 Torr
- Chuck Brock has some design
- Ann: pressure controlled on PALMS, will talk to them to borrow design
- Sensitivity corrections, gain of the multiplier changes with time, need to take into account sensitivity changes, John measured before and after flight
- Heater bias suddenly changes by several volts, need to separate them, solution to have a system keeping lens at optimum pressure

Johannes: DLR Falcon

- Up to 12 km altitude
- AMS, MS (Arnold), DMA, CO2
- Two racks
- Quad down, inlet outside, go thru other rack, $3k aluminum, withstand 9 G forces
- John: make sure SS of quad is directly bolted to the Al frame
- Johannes: need to prove every single part of it will withstand
- John: wire shock mounts
- Johannes: whole rack will be shock mounted
- Jose: vibration wasn't bad, truck worse
- In the air, not bad, worst during takeoff and landing

Next Flights

- Johannes: Flying March 2003
- John: G-1 Mexico City April 2003
- Jose: No plans for the Twin Otter
- Hugh: UMIST test flights in March 2003 (optimistic), actual date is moving target.
- Ann: P3 Summer 2004
- John: rack mounted with buried inside somewhere

Keith: Rack System

- Electronics on the bottom
- Hugh: met office used to fly with perk(?) racks, this is 9 G forward, 6 G back, 2 G side, AMS swappable with that in mind, operating for on port, or aft on starboard?
- Quad suspended from horizontal beams in the middle of the rack, Barry(?) mounted, aircraft approved mounts, 4 places on top, 4 on bottom, plate for CPC and RF box on top
- Can't protrude on walkway side, pretty flush against cabin wall
- Power 110 V, 400 Hz, switchible power key, straight into power system
- John: Is 400 Hz OK? Computer is questionable. Main bits OK.
- Computer is 47 to 63 Hz
- Balzers is also 47 to 63 Hz
- John's components go to 440 Hz.
- Transformer on board. Maybe a UPS will do this?

Frank: Intercomparison of Semi-continuous instruments in NY

- R&P 8400S, Hering ambient particulate sulfate monitor, denuder, RH-controlled, impacted on heater, flash vaporize in SO2 analyzer, 10 minutes
- HSPH continuous sulfate monitor, PM2.5 cyclone, denuder, tube furnace w/SO2 analyzer, averaged for 10 min
- PILS no PM2.5 cut point, denuder, condense water and impact, goes into IC system
- Also some filter samples, 6 hr and 24 hr at Queen's College, 24 hr at public school

Sampling at Queens College

- Different sampling inlets for filters and semi-cont instruments.
- Overview of all the data
- Correlation plots, all SC compared to PILS, all the slopes close to 1, R2 > 0.9, recovery ~1, intercept forced to zero
- Filter samples, slopes close to 1, R2 > 0.97, recoveries 0.97 to 1.08, 6 hr about 6% higher than 24 hr.
- Typically see less sulfate compared to the filters, incomplete sampling of PM2.5, 100 nm cutoff for R&P, AMS inlet transmission, PILS losses for large particles and small unactivated particles, 2-10% less. HSPH conversion loss 5%
- Filters shorter inlet lines, filter artifacts, one had denuder but not corrected for blanks,
- Filter samplers had regular cyclones, not a very sharp cutoff, still measure 10% at 5 microns, filter collects everything. AMS and PILS had cyclones, but intrinsic inlet cut points. Other SC had sharp cut cyclones. Also possible oxidation on the filters
- Doug: what does the TEOM sample?
- It had a PM2.5 sharp-cut cyclone. Not made by URG, R&P.

Nitrate Intercomparisons

- R&P 8400 N
- AMS
- PILS
- 24-hr filters
- Time series messy, but typically PILS has the highest concentrations, AMS smaller, R&P significantly smaller

Nitrate Comparisons

- Slopes vs. PILS, after scaling with 2.34, AMS 0.87, RP 0.57
- Jose: Houston events externally mixed
- Doug: most of Houston data need the same scaling factor
- Slopes vs. Filters about 90%
- Losses caused by non-complete sampling of PM2.5, RP decrease in efficiency of Mo converter
- Jose: nitrate events in the morning CF=1
- James: Pacific nitrate correction factor of 1, comparison with filters was consistently good

Discussion

- Jose: correction factor depends on shape, particle focusing stayed constant, better than it is
- Manjula: sulfate constant, internally mixed.
- Doug: put up the size distribution, with statistics to look at variability
- John: table of scaling factors
- Frank: putting in size distribution
- Doug: Vancouver data make that same plot
- Jose: summarize, 2.3 factor shape dependent effect, same for all populations/modes of particles (internally or externally)
- Doug: close the mass pie chart, how do we interpret pie chart, 36% rest, sulfate, nitrate, and ammonium normalized to PILS, size determined by the TEOM (agrees with filters), 15% discrepancy between PILS and filters.
- Frank: not all because mass, filter loses nitrate
- Doug: if we can account for roughly half of 36%, 10% is BC and dust, 2-5% inlet losses in the 15%.
- Frank: filter sulfate is 85%
- Doug: disagree with error because AMS scaled with the PILS, within 10% or so, do we think we have mass closure?
- Frank: organics
- Doug: next point, organics, nitrate and ammonium looks pretty good, organic size distribution is different, shift in size distribution relative to sulfate, organics undetermined with pie chart, some of the organic should be scaled by PM2.5

Discussion, contd.

- Hugh: assume internally mixed, get upper bound. Fit distribution.
- Frank: not necessarily, assumes 2.34 accounts for large particles, but nitrate in Houston is 1
- Manjula: pure nitrate particles, no sulfate
- Frank: not focused as good
- Hugh: basis of agreement with PILS
- Doug: issue is 2.34 contains two processes: large particles lost at critical orifice, nonspherical particles not focused, no way of quantifying which is which (beam profiling), bounce detected by multiple bounces in TOF trace, second order effect in new oven design, large particle transmission will depend on particle type, in NYC data is 2.34, in the Houston data is 1.9 or 1.8, reason is Frank saw larger particles, shifted to the right compared to Houston
- Jose: spike in nitrate has different size distribution than sulfate, try to look for different populations
- John: small mode organics in Houston are secondary, NYC more likely primary aerosol, soot with adsorbed OC
- Jose: going on the surface area mode
- Hugh: morphology
- Ann: constrain Organic with other measurements
- Doug: come a long way from last year

Summarize Different Factors

	nitrate	sulfate	organics	ammonium
1) IE	1	0.87	0.7	4.5
2) Fragments unmeasured	TBD	TBD	TBD	TBD
3A) Collection/ shape, divergence of beam	1, if externally mixed with sulfate Or same as sulfate, if internally mixed	NYC 2.34 Houston 1.7 Flight 2.5 Vancouver 1.7-1.8 Ron Brown 2.2	Small mode: Use 1 if externally mixed, unless soot-derived, same as sulfate if internally Accumulation mode: internally mixed same as sulfate, not if shifted to smaller sizes	
3B) Size cut of lens, different for each lens, f(size distribution)				

Discussion

- Manjula: compare with MOUDI
- Doug: mandate size efficiency factor, divergence factor, explicitly separate them?
- John: yes
- Doug: physical reason for losses before and after the lens, use size distribution to do closure
- Thomas: constant or controlled conditions, check TSI DMA, CPC independently, APS difference within 5%, get sulfate mass overall, convert with calculations, only thing is to run AMS, Dutch guys developing total dissolved carbon, OK with stable reference system, not field measurements where it's unstable.
- John: this is what the user's meeting is about, framework for doing those types of studies
- Ann: refractory material, different ambient sampling environments
- Thomas: use the stable data to compare

Sept. 2002

- Comparisons with MOUDI from Pittsburg
- Looks very close
- S-M Li: MOUDI sample need to be careful to invert data, issues of particle bouncing

Not AMS

- Stuff we don't measure:
- Crustal/metals 5%,
- BC 5%,
- refractory salts (NaCl, sea salts, mineral sulfate, etc.)
- Water, lose 60%, measured 40%, based on lab studies with sulfuric acid, need to do it for ammonium nitrate, ammonium sulfate
- Scaling factor for organics
- Frank: multiply for the 15% lost, then the pie is full (Doug's point)
- Doug: water is not 0 on TEOM
- Ann: SVOC?
- Frank: used new differential TEOM, agreed well with the other ones, so SVOC minor fraction of the total mass

Other instrument issues

- PILS is low
- Cyclone/cut points (5-10% loss of filters compared to PILS)
- Line losses for PILS
- Frank: correction factor determined with filter, not PILS
- Manjula: sulfate filter and sulfate PILS compared well in Houston, depends on sulfate mass above 2.5 micron
- Jose: Teflon filters, not quartz
- Doug: 9 lpm throwing away, routinely put in filters and measure sulfate, doesn't cost much to collect
- John: simple, colorimetric tests for filters?
- Doug: doesn't exist at this level, need IC
- Jose: need to be better than a factor of two, otherwise useless
- Filter, TEOM, MOUDI have artifacts, volatile losses or gains, reaction of species during sampling

Phil: AMS vs. NIST spectra

- How comparable?
- Systematic biases?
- Affect on organic analysis?

Examples

- Anthracene m/z 178 parent also seen with AMS (best case)
- Succinic acid m/z 100 parent, still pulled out of NIST search, AMS biased toward lower fragment masses than NIST, plus thermal decomposition making 18 and 44.
- Bigger issue as more oxygenated (malic acid) almost all 44 and 18 in AMS spectra.

Correlation Plots

- Anthracene spectral intensity coded as a function of m/z, follows close to 1:1 line
- Oleic acid lower masses not as well correlated
- Dicarboxylic acids are worst.

Plot of 44/total signal vs. #C

- Roughly 9* 44 than compared to NIST
- Look as f(O/C) ratio, water may also be important, compounds with more water give less CO2, take CO2 and H2O together as indicator, get pretty good correlation with O/C.
- Doug: Average 44 slope, equal amount of the particle CO2 signal is appearing as water, get estimate of how much water could be from thermal decomposition of organics (small fraction). Maybe add into organic mass.

Summary

- Aromatics close agreement
- Heavily fragmented species get more signal at lower m/z
- Oxygenated compounds thermally decompose into H2O and CO2
- Frank: temperature?
- Hugh: peak of sensitivity as f(T) always around 550 C
- Frank: relative m/z 44 as f(T)?
- Hugh: yes
- Doug: can't be simply decomposition, not enough CO2 in molecule to give such high signals, actually fragmentation after ionization, put lots of oxygen into C-analyzers, so not like them
- S-M Li: analysis for short molecules, except anthracene, still see a lot of CO2 with longer molecules?
- Phil: 44 lesser contributor to total mass for C9 molecule
- S-M Li: obviously see a lot of that
- Doug: mass 44 (CO2+) most important organic component in the field, and also 43 (acetate)
- Jose: paper by Paul Ziemann decomposition into smaller fragments

Jose's Worksheets: Initial checks

- Provide a general one and one for new users
- Webpage utility for network Atomic clock
- James: save times get screwed up, two clocks (Windows and computer), Windows update
- John: separate PCI card for clock
- Doug: drift is temp-dependent
- James: clock slows down (temp effect?)
- Save electronic file of computer screen printouts
- Space left on hard drive
- Antivirus check, run before campaign, plus defrag
- Airplane, weather affects flow rate, Weather Service has website to calibration Baratron
- Flow meter not very sensitive, pressure inside the lens is important and needs to be calibrated, drifts due to calibration drift or ambient P drift
- Check inlet flow, critical orifice clogged, Gillibrator works, dry cal has problems due to significant pressure drop, calibrate DMA too ($2500)
- Thomas: correction for water vapor on the order of the vapor pressure

Vacuum checks

- Health of the vacuum system, run thru at the beginning of the campaign, condensed daily version
- Pump speed and current, current increases as failing before pump actually fails, inlet closed and open
- Lens pressure is diagnostic if the lens is clogged, more precise than flow meter
- Ann: depends on met conditions
- Jose: look at it and determine if it's meaningful
- James: best hit light on the RF box, Balzers manual wasn't flashing on the fault line
- Jose: uses a little bit more power when flashing, but OK

Performance Checks

- Software version kept in the files
- Always write in systematic way then other people can see it, e.g. Houston data didn't keep track, can't remember.
- Slow board analog voltages, make sure working
- Switches for the electronics
- Measure electronic noise, everything on but filament and multiplier off
- James: routinely run scanning m/z 11 in TOF mode, shouldn't detect ions there, so all electronic noise, useful in ITCT by measuring it, take out chopper interferences
- Jose: numbers not meaningful when running, so good idea (James), depends on fast board sampling rate

Performance Checks, contd.

- Balzers error messages, see manual
- Cross check resolution and mass scale calibration, default corrects this in use between saves, still check it! Can recover from MS but not from TOF.
- Doug: F6 window look at 28, 44 peaks
- Jose: sometimes the serial box gets confused, restart program to fix
- Offset parameter in the F6 window should be the same for all the masses
- Check that there is a MS!
- James: only really update it if significantly shifted
- Jose: don't tune the AMS unless really have to
- Heater setting, look at the temperature (increase for PSLs, forget to decrease)
- Tune ionizer, paying attention to m/z using (28 or 32 and not 18), 28 better if chopper opened, any peak (background, particle, etc.) with chopper closed was old test, seemed to be OK
- Manjula: newest version tunes with it open, but no one has it yet
- Doug: Bold font for mass used!
- Jose: paste whole thing into PowerPoint
- James: old, new, difference in bits or percent is gone, which one?
- Manjula: will check that
- Doug: new ionizer control module, beginning of the mission, after stable, tune it 6 times in a row, walk better to optimal voltages.

Performance Checks, contd.

- Calibrate multiplier, make sure threshold is set OK, could have a problem with dark current generating noise
- Doug: real question criteria for setting gain, not the knee, but how much signal you have, look at the signal you have to determine voltage you want
- Jose: change from yesterday, kind of big (32%), save screen in PowerPoint
- Doug: real issue … in MS mode, full scale for the data acquisition board, the 28 signal is about 2/3 of full scale, too high uses up multiplier faster, too low run out of dynamic range for big particles, change the multiplier voltage to get signal you want then go back into EM cal and by definition the middle voltage is the one you were set at, decide based on that if you need to make a change.
- Jose: Disagree - don't need to keep 28 on scale, can use 32, Measurement of the gain is wrong, want to be on the knee or higher, otherwise measurements can be biased.
- Doug: changing the criteria, this instrument has the lowest water vapor I've ever seen, want to know how close to saturation you are.
- James: example, threshold too high because no knee, try setting voltage with the preamplifier turned off, then the shape of the curve changes with knee at lower voltage.
- Jose: see the same curve at higher voltage if higher threshold, sometimes the dark current from multiplier could affect it.
- John: Balzers multipliers have the dark count, ETP doesn't, depends on the Balzers multiplier, better get a spare ETP.
- Doug: Balzers can't keep on the shelf indefinitely
- John: ETP can be there a year or more, made from different technology, Balzers copper beryllium
- Doug: failure of multipliers is increase in the dark current.
- Jose: multiplier on/off with background mass look at the threshold

Performance Checks, contd.

- Jose: make sure AB is not saturated
- Doug: disagree, measure AB and calibration with ammonium nitrate particles under conditions where the gain is defined, if the gain drifts, IE should scale with AB, trend in AB over time, won't know if something is changed or if EM cal is changed, procedure is not fool-proof
- Jose: agree in general, but AB takes care of it, funny problems, different failure modes
- Ann: higher gain, EM shorter lifetime
- Doug: absolute signal look at full scale
- John: talk about bits not Hz (which includes gain)

Performance Checks, contd.

- Check air beam with summary window, toggle mode
- Molecular velocity dependence on MW in air beam – John and Eiko measured.
- Doug: current versions of software crashes due to operators, exit program after calibrations and restart program
- Jose: check repeatability of EM cal
- If AB is strange, check servo motor (not common anymore, but still fails), want open position at peak (center).
- John: failures? Just Jose, Vancouver didn't actually fail but was replaced
- David (CEH): Group members in TOF window, needed 28 as B, 32 is another letter, I is for EM cal, can only have one m/z as "B"
- Jose: TOF AB and MS AB should be similar
- Displaying too often reduces duty cycle
- David (CEH): chopper freq is red, warning?
- Jose: always pay attention to red warnings, in this case, chopper speed is too fast for maximum diameter
- Check that the chopper is not being simulated, set chopper speed control to automatic, otherwise it may oscillate
- Keep track of heater bias on the multiplier on the electronics box

Jose: Calibration with NH4NO3

- Go thru standard steps for calibration
- John: threshold routine too low with the magnets, manually make them higher
- Jose: increase the width of the single particles
- James: how do you remove noise?
- Manjula: hit "N" in stick mode to remove calculated noise, questions about how that is done, make automatically updated, now it's not

Running James' Program

- Doug: the FUN part!
- Loaded the data, nothing else, haven't looked at the data set (Pittsburgh)
- Invoke corrections and auto updates are off
- Look at diagnostics (no MS AB)
- Duty cycle trace, should be around 84%
- Lose some by switching between modes, NYC alternate mode brings up duty cycle
- Jose: want to have at least 80%
- Corrections window – turn all off
- Choose AB reference period, calculate AB corrections
- John: why recalculate errors? Not apply them?
- Doug: that's what I'm trying to go thru when it decided to crash, do each one by one, don't use as a black box
- After reboot, forgot to pick the window for AB reference period

James' Program

- AB signal down with time, recalibrated EM
- Ideal case, recalibration causes correction factor to return to 1.
- Next recalculate sticks, look at noise in the correction factor to see if any spikes in the noise caused drifting, in this case no
- James: this version of the code had a bug in that routine (recalculate sticks), so it didn't do it
- Doug: do correction for the flow rate, relatively small effect
- Finally, smooth it by 4-5 points and recalculate one more time
- James: measured variations in the strength of the AB signal, due to variations in the flow rate, replacing pinhole with a needle valve, AB varies linearly with flow rate with an offset, makes it more correct, but not a big correction for a ground site
- Jose: changes in the m/z calibration of the quad, temperature changes in the RF box, try to keep that constant, only correcting every time it saves, so keep that in mind.
- Doug: one minor comment, make sure you miss a save whenever you do something to create a gap in the dataset, to indicate that something happened.

James' Program

- Mass Spec time series, turn off scale to AB, time trend of all the species classified
- Thicken lines and add legend
- Various events,
- Next scale to AB, be aware of how large the corrections are.
- MS Average, scale to AB, MSSDiff, plot new graph, add negative, log scale
- One by one go thru species
- On time trend graph look at ammonium divided by sulfate. Lowest loading for ammonium (16 O+) not corrected from AB correctly. So need to go to the batch waves.
- Jose: filter on inlet periodically to check O+ signal in 16.
- Doug: all those traces' colors came from batch file, AB, etc. defined. Fragment list has how species are determined from m/z. Scaling factor is at the end of the batch file. Going to the fragment waves.
- E.g. 28 is only for air, 14 is only for air, 15 from N15 in air is 0.004 times signal at 14. Isotopes are put in here.
- Discussion about 30 – contribution of organics to 30 and organic nitrate
- S-M Li: will be doing lab studies looking at fragmentation pattern
- Doug: grey in MS is from air, colors determined by fragmentation pattern, CO2+ is from the particles, accounting for the air, atmospheric CO2 could become very important, go thru and check the fragmentation patterns

James' Program

- Sulfate example: only assigned major peaks, 48 SO+, 50 has S34 isotope, 64 is SO2+, assuming the sulfate at 48 is leftover after subtracting organic contribution to 48, calculate 50 from S34 isotope of 48, etc., 80 is SO3+, 81 is HSO3+, red is the contribution of sulfate to the signal at that mass
- Delta pattern is underneath the sulfate pattern, 48 from organics is low because it's in the trough of the delta pattern, not set up to completely analyze this properly, agrees well with everything Frank talked about for the fragmentation pattern of sulfate,
- Based on Frank's measurements we can estimate, 65 Frank is seeing HSO2+ fragment which is 5.7% of 64.
- Recalculate with new 65 for sulfate. Need to subtract 65 sulfate from organic (frag_organic=65,-frag_sulphate[65])
- Idea is to go thru this systematically and convince yourself that you are calculating the right things.
- Other major change with fragmentation list is 25% of sulfate is coming from water. Referenced to 64, 18 =78.16% of 64.
- Hugh: nothing to stop the user from creating circular arguments
- Jose: check peaks up to 100%
- James: OK, put that in
- James: program checks batch list and evaluates everything until it can identify everything by the appropriate m/zs

James' Program

- Calculated sulfate contribution to water at 16, 17, and 18
- Look at the ammonia pattern, ammonium appeared too high, immediately sees that the fragmentation pattern from ammonia (NH+, NH2+, NH3+) the ratio from Frank is 1.1*16? Problem is the correction for O+ at 16 is not enough (completely empirical), but can be measured with a filter or go to the mass loading.
- Forced the ammonium sulfate ratio to be 0.3, make this correction
- Ann: disagree with forcing because don't know that ammonium sulfate is present in the ambient air
- Eiko: go to time of flight mode? Doug: Yes
- John: multiply 16 air signal by 1.3
- Doug: not the best or the only way to do this, completely empirical
- Manjula: check the right fragmentation pattern in the ammonium nitrate pattern
- Jose: pure water, filter, hard because using nitrate like crazy and keep it clean, in principle it can be done
- Doug: procedure is justification for doing a filter, argue that it doesn't work is when there is a problem in 16, 17, 18. Self-consistently getting ammonium and sulfate.
- Thomas: no nitrate in the aerosol, then the ammonium sulfate is not necessarily neutralized. How would it look if ammonium bisulfate is measured?
- Ann: also organic acids neutralized by ammonia
- Doug: this procedure is not the definitive one, not by coincidence getting the right fragmentation pattern of ammonia. Do filter measurement for at least an hour.
- Jose: get fragmentation pattern
- John: add procedure that verifies everything adds up to 100%
- James: will also add warning about circular logic
- Doug: see change in fragmentation pattern if not ammonium sulfate. Should look like Frank's pattern, looking at the water signal there's no way we can say anything about the fragmentation pattern. Ratio 48, 64, etc.
- Eiko: distinguishing different composition ratios
- Doug: macro to calculate sulfate fragmentation pattern.

James' Program: Batch file

- Water fragmentation pattern
- 18, less small correction for O18, and sulfate 18
- James: Artificially subtracted sulfate from water at 16, and 17
- Hugh: nightmare!
- Doug: correct for organics in sulfate pattern
- Ann: described how to do it by averaging +/- 14 amu from peaks for organic contribution
- Jose: James' program is now making it easier to calculate consistently
- Ann: now need to do it for 30 (organic contribution)
- Phil: only contribution of organics to 30 is from amines
- James: can come up with a few routines to help diagnose issues with batch file
- Doug: share the lists to combine what we are doing, check the fragments for each instrument/dataset. Go to the mass spectrum and force the 16/17 ratio to be correct.
- John: Likely the filter zero needs to be redone every time you tune the ionizer.
- Doug: next really important concept, exception of not adding m/z 32, added all the fragments of sulfate from Frank
- Rename calibration factor column as ionization efficiency relative to nitrate (James said, technically it's the reciprocal of that). Define this appropriately then only the laboratory determined ionization efficiencies are put in here.
- Difference between what we are doing and what Frank is doing is by including the organic contributions.

James' Program

- Batch file - Scaling factor for sulfate is 1.47/1.9? (didn't follow Doug here)
- Eiko: different calibration factors for TOF data?
- Doug: no, reason for normalizing TOF data to MS data
- TOF all species average for whole mission (put in run numbers), don't normalize to MS, scale to MS AB and TOF AB

Manjula: Analysis of Organics

- No separation of individual species prior to vaporization and ionization
- Overlapping patterns of multiple molecules
- Examine time trends and size distributions
- Example: 48 and 64, organic class1 (44) and class2 (55 and 57)
- Correlations of fragments with other species in the gas phase
- Example: 44 and 43 signatures of oxidized species in the aerosol with PAN, PILS ammonium, etc.

Analysis of Organics

- Marker for oxygenated organics is 44
- Hydrocarbons have long envelope with a bunch of peaks separated with a regular pattern, characteristic of specific species (like fluorocarbon oil contamination)

Delta Analysis: Ion Series in Mass Spectra

- See McLafferty and Turecek, “Interpretation of Mass Spectra”
- R-CH2-CH2-CH3
- CH2 groups form backbone of molecule, generates a series of fragments separated by 14 amu
- delta = peak mass -14n+1
- Different deltas correspond to different types of organic compounds (unsaturated aromatics have deltas of -4, -5, -6)
- Clustering of different types of compounds, deltas do not correspond to specific groups, but may be used to distinguish different degrees of saturation/oxidation

Example of Delta Patterns

- Delta = 2 (alkane), e.g.. 29, 43, etc
- Delta = 0 (increasingly unsaturated) 27, 41, etc
- ARI lab spectrum of pentacosane (long chain HC), strongest contribution is to the delta 2 group
- Aromatic dicarboxylic acid (phthalic acid)
- Add up all the fragments that correspond to a delta value and determining their relative contribution to total organic signal.
- Maleic acid (C4 unsaturated acid) biggest delta contribution is -1
- Malonic acid (C4 dicarboxylic acid) largest component is from delta 3, indicative of oxidation
- 44 ions from dicarboxylic acids, all give large delta 3
- Black shows the percent of 43 that is in delta 2 and percent of 44 that is in delta 3.

Diesel Fuel Example

- Diesel fuel, show entire spectrum with different colors for different delta groups,
- Intensities as a function of increasing carbon numbers (try to make sense of envelope). Straight line slopes didn't fully characterize fall off with increasing c-number, do a fit to describe it. (fall off plot)
- Composition is pink for other (= 15, 16, 17, 18, etc.), green for organic.
- 44 and 43 are included in fall off plot.
- Doug: diesel fuel looks like delta 2, but also contains delta 0, in HC 43 is a small part of delta 2, small delta -2.
- Jose: decays linear in log space (Ann: small effect when subtracting averages, Doug: no log in batch file of James' program)
- Jose: other comment spectra from McLafferty

Diesel Discussion

- Hacene: 2x unsaturated?
- Manjula: no, because cycloalkanes can have delta 0 and some alkanes have some delta 0
- Doug: rather than unsaturation, this could be branching (cycloalkane is the extreme).
- Manjula: more unsaturations, lower in the scale
- More heteroatoms, higher in the scale
- Jose: this way it represents loss of H
- Manjula: it's as though you add hydrogens
- Doug: alkanes can't give any signal here (delta bigger than 2 or 3)
- For delta =3, subtract C13
- Dave is right that it's C13 (maybe)
- Qi: How to get the delta 2?
- Add all the peaks that generate a delta 2 value together and divide by the total organic signal to get relative delta 2 signal.
- Keith: why assume CH2 and not functional group?
- Jose: that's why 43 and 57 show up.
- Doug: not assuming anything
- Phil: knocking off CH2 makes sense for long chain molecules, but got to be careful for organics with lots of functional groups.
- James: Rami's work, functional group is bimodal in the delta pattern.
- Manjula: what is the most common part of the delta pattern? Do a bunch of lab experiments to determine that. Or go to sources …

Other Combustion Sources

- Aircraft exhaust: delta 2, 0, and -2
- Eiko: what was combusted?
- James: how did you make it?
- Manjula: Nebulize, sometimes in hexane.
- Twin Otter exhaust: mainly 0, 2, relative ratios are different from other aircraft exhaust
- Ship Plume UMIST: 0, 2, -2 on top of ambient data (Jeff Brooks bringing emission info together for Pacific study, Eric Williams for NEAQS2002)
- Winter and summer Manchester pollution: look very similar, except winter has more 0 than 2 and summer has equal 0 and 2, early morning data not affected by photochemistry (rush hour), locally dominated pollution – qualitatively similar
- CEH Edinburgh: natural gas heating morning peaks, own building, similar delta 2, 0, -2 slightly different ratios
- Prophet: organic only event diesel? Afternoon delta 2 dominant, then delta 0 and 3 comparable

Photochemistry

- Houston: 43 is shooting up
- Aged plumes (UMIST, Cheju-Do): 43 is really big (delta 3) then 0 and 2.
- Pacific (UMIST): (went by too fast)
- Crete (Mainz): sources 1-2 days away, again 43 (delta 3) is really big, also see 0, -2, and 2, chain length may be shorter because fall off is sharper.
- Note that all the fragments of sulfate (and other organics) have been taken out in calculating the deltas.
- Write procedures to calculate delta pattern functions. Own little panel that comes up. Makes delta fragment waves in batch file, copies element over from organic fragment wave in James' program, calculate time trend as f(time) and can also get the average delta pattern and colorize mass spec average. Way to incorporate into James' program.
- What Frank has done … Delta 0 and Delta 2 patterns as f(TOD) in NYC (0 high in morning, 2 high in afternoon)

Delta Pattern Discussion

- David: All these 70 eV spectra?
- Doug: Can do whatever you want but lose some intensity.
- S-M Li: how well can you separate?
- Doug: add delta 3 and 4 are oxygenated, glib assumption that amines are negligible
- Houston photochemistry data: hard to know how to quantify these, fraction above delta 0 is rather large, long chain will give lots of HC peaks, qualitatively Mainz delta 3 is the signature of oxygenated organics. Aromatics show up down here (-7, - 5, -3), 77, 91 and 105 unmistakably aromatic.
- S-M Li: sulfur containing compounds,
- Manjula: heteroatoms will pull it up
- Jose: many heteroatoms will loop it around the delta pattern, consistent with it being hydrocarbon, but not it is HC.
- Manjula: plan is to do this for a bunch of lab species and NIST spectra
- Hugh: Rami's made a start of this, HCs and oxidized organics, can't do organic nitrates
- S-M Li: halocarbons too
- Jose: Important to publish!

Jon: Brief Discussion of HDF

- HDF new format, doesn't save the redundant data, space savings isn't all that big, can put into Mat Lab or other database program
- James: big advantage is the random access
- Catalog of itx files
- Manjula: will send out email again

Aerosol Sampling in Prophet

- From "sampling and transport of aerosols" John Brockman
- Aerosol parameters:
- Relaxation time, settling velocity, stokes number
- Plot of relaxation time vs. Da
- Sampling from ambient into still air
- List of avoidable/negligible sampling losses

Aerosol Transformation

- Not covered well by Brockman, interested in the chemistry of particle
- List of issues
- Gas wall loss includes diffusional and turbulent loss of gases, can also have out gassing, contaminated tubing not important for bulk measurements
- Diffusional losses, lower for laminar flow with Re as close to 2000 as we are comfortable with

Prophet Tower

- Three inlets
- Used ½" tubing, cyclone, gentle copper tube bend and down the tower
- 12 lpm flow rate total with isokinetic take off, most of the flow goes out critical orifice, radial heterogeneity introduced by long lag time, so passively mixed flow, then another isokinetic take off for SMPS and AMS.
- Remove large particles, laminar flow, large excess flow, passive flow control, mixing is questionable, temperature control lines, residence of the centerline was 10 s.
- Tested by generating particles, measure w/ CPC, and then put into inlet, losses probably due to mixing.

Discussion

- Richard: losses? Low flow thru something with sharp corners could cause dead spots.
- Johannes: problems with copper tubing?
- At least a day's trajectory from acidic particles, for logistic reasons couldn't use SS.
- James: mixing down pipe, temporal broadening?
- Parabola on the centerline for laminar flow, so very little temporal broadening.
- James: flows around corners?
- Radius for turns at least 4 feet.
- Richard: evidence of biogenic?
- Alice: maybe, but not a lot.

Jose: Web Page

- Old: www.its.caltech.edu/~jljimene/
- New: www.cires.colorado.edu/~jjose/ams.html ?
- Copies of users' meeting files
- Central repository of papers and conference presentations
- Research groups and links, including other types of particle mass spec groups
- User's meetings
- Pictures of the AMS
- Other resources, including manuals and other information

Complementary Instruments

- What are most complementary?
- Will depend on application, make sure properly operated and calibrated
- Fast instruments of things we don't measure
- Slow instruments that enrich the interpretation
- Jose's List of Fast measurements:
- Hugh: Pandis group SMPS system, couple APS system to it because no aerosol number at the top end of the accumulation mode
- Jose: get Don Collins involved
- Eiko: MOUDI huge nitrate issue, online IC with different impactor size cuts
- Jose: first approximation, use MOUDI for sulfate
- Frank: prefer differential TEOM, one filter and ESP to turn aerosol flow on and off, correct for evaporation of the volatile stuff.
- Get around PILS if we ramp the heater temperature.
- John: small photoelectric probes for PAHs
- Phil: comparisons with the ELPI
- Manjula: higher stages get contaminated by the smaller particles
- Other groups have problems with this instrument
- EC/OC continuous analysis, still new, some correlation with organics
- Rodney's new TOC instrument

- Comparison of Commercial AMSs shown in tutorial

Aerosol Climatology

- Try to have a draft before the next user's meeting
- Hugh/John: don't think it's too early, themes that run across the data sets
- James: nail technical problems
- Doug: don't believe that that's an issue, issue of what we miss compared to 2.5 is not important
- Hugh: remote vs. urban, if nothing else it provides us with some kind of harmonization across the groups, thinks that by next year those things will be addressed.
- Jose: start first draft and circulate, give him presentations.
- James: proposing that Jose would be the first author on it?
- S-M Li: special issue somewhere and use this paper as an umbrella
- Jose: special session at AAAR was not focused
- James: get other papers out, better if with special issues for each campaign
- Jose: include the ones that have already been written up

Doug: Comparison of predicted NH4 to calculated NH4

- Pittsburgh: Looks like fully neutralized ammonium sulfate and nitrate, high organics, maybe some excess ammonium
- Jose: sulfate plumes that were not fully neutralized, still see regional aerosol
- Not allowed to use the command line!
- James to do: Time trend, mass spectrum, image plot of size distribution, size distribution all in one macro (delta pattern and average concentrations)

Doug: Clarification …

- Vaporizing everything at the same time
- Separation of organics and inorganics and what we can say about them
- Colors on MS attempt to separate organics and inorganics (fairly straightforward)
- All inorganic fragmentation patterns are understandable (solved problem, make sure it's implemented properly)
- I need to write a tutorial! We need to somehow build an editor to check that table.
- Next order issue: what do we do with all this green – organics (Manjula, talking about delta analysis), all the organics at the same time. Delta analysis is really the first cut, want to get specific compounds. Old version of James' program is in units of Hz, want ng m-3. Any GC/MS analysis of individual compounds ng m-3 or 10s of ng m-3 (about X Hz). Parent ion is small fraction of the total signal, ideal world 1% of the signal is in the parent ion, 1 ng m-3, small signal mixed with everything else at once. Impossible to speciate individual organic molecules. To compare to literature, how many ng m-3 do you really expect to see, will you have any chance of seeing it in terms of percentages of the total – complex problem, to say the least!
- Review MS and delta analysis from yesterday (first cut) – show Manchester winder data. Basically the ratio of all the deltas greater than 2 to the other reflects the degree of heteroatoms to the rest of the molecule. The ratio isn't precise, as Jose mentioned, see alkyl chain in the fragmentation pattern. Combustion aerosol and processed aerosol.
- Example from CEH group (building exhaust) – ratio of oxygenated is somewhat different, but picket fence goes out to higher masses (Ann: may not have enough signal for the Manchester data). Real point is the delta pattern ignores that, so really only started to look at that information. Degree of structure is important, but difficult to interpret. We as a group need to deal with this. We are going to figure it out by making these measurements and combine them with others. Clearly seeing systematic similarities and differences. Framework for comparing them. Hopefully next year we will have a clearer and more defined version of what we did yesterday.

John: G-1 data

- DOE SBIR to upgrade aerosol measurement capability on the G1 aircraft
- Background of the study – New England Air Quality Study
- Show the package for the AMS, specified rack system, everything else up to them
- Aerosol inlet designed by Fred Brechtel, double diffuser cone with actively flow controlled MFC.
- S-M Li: inlet, sample with pump and T?
- John: no pump, but Venturi pumped, adjusted velocity to match plane speed with MFC
- S-M Li: design from Fred?
- Talk to Fred! Doug: potentially practical and useful design, one flight speed (400 knots, 100 mph?)
- G1: Twin turbo prop, room inside to stand up, but tight and hot

Sample data from July 22

- Showed all the data
- Blow up of AMS date & time trace of sulfate (up to 60 microg m-3) and size distribution
- SO2 sometimes nicely correlated with sulfate, sometimes not
- HYSPLIT model predicts air came from Ohio Valley
- Blow up of GIZMO plot (longitude, latitude, altitude) with sulfate mass loading
- Nice to develop as we go along
- Data not corrected for changes in inlet flow

Hugh: UMIST Studies

- Long list of 8 campaigns in the past two years, starting with Edinburgh, Nov 2000, ending with NAMBLEX, Ireland, Aug 2002
- James' thesis on urban studies
- Also looking at various cloud/aerosol interactions
- NAMBLEX – chamber studies with seaweed

Winter in Manchester

- Studied two periods with different modes of organic aerosol, low winds and high winds
- Low winds, stable air, pollution develops over a number of days, very common
- Looked at back trajectories, power stations to the south, southwest, never see sulfate when the back trajectories are not from that area

Summer in Manchester

- High activity and low activity periods
- Winds from the south (high activity) and continental outflow (low activity)
- Fragmentation analysis looking at the modes of different species
- One large accumulation mode (600 nm) for 44 (Delta3), 45 (Delta4), two modes for 43, higher smaller mode (100 nm) for 55 and 57
- Weighted size distribution for organics, organic distribution is skewed if you don't pick the right peaks.
- Doug: note that the 44 and 45 …
- Only need to count three masses to account for most of the variability

ACE-Asia

- Comparisons with impactors, only recently been able to do this
- Haven't looked at the sulfate scaling factors based on the impactors at this point
- Saw three types of aerosol: China, Korea, MBL (aged)
- Also saw nitrate in impactor samples that the AMS didn't see, associated with the coarse mode
- Sulfate not too bad
- Focus on Stage 1 of Berner with AMS 0.2-0.5 microns
- Haven't folded Frank's new factors in here, but sulfate OK, nitrate looks very good
- Water soluble organic
- James: nitrate loading in the accumulation mode might have organic interference
- Looked at 30 and 46 fragmentation pattern as f(Da), ratio 30/46 about 3:1 in accumulation mode, above 1000 nm the ratio is much higher. See significant amounts of this material despite the lens transmission. Clearly refractory material has higher 30/46 ratios than ammonium nitrate.
- Doug: really vaporizing HNO3 with ammonium nitrate, CaNO3 makes NO, NO2, leave Ca2O on the oven (similar with NaNO3), so there's a really good chemical reason for why this happens.
- Jose: signal above 2000 nm, PM10 impactor on the inlet
- Hugh: more nitrate than sulfate, but it's all in the coarse mode
- Doug: orifice clogging? No

Jungfraujoch 12000 ft

- AMS, CPC, OPC, DMPS, Carbon, HTDMA in ethylene glycol
- Heated inlet to drive off cloud water from residual aerosol, then take in all of the aerosol
- Other inlet PM1 on the end, no cloud droplets
- Inlets switched every 10 minutes

Jungfraujoch Data

- Summary from total period
- Very little from the local pollution
- Shift in the organic size distribution to the lowest size
- Predominantly 43, 44, 57 in the accumulation mode
- Inlet differences, plotted with cloud droplet number, for nitrate, sulfate, nice cancellation when the droplet number falls
- Reduction of 43 and 44, need to look at more thoroughly
- Some evidence of activation differences for different species in different or similar modes: nitrate, organics, sulfate, a lot of explanations
- Complicated because advected synoptic system over the site with vigorous updraft velocity, both processes could account for the differences in activation of different species, organics and nitrate from upslope, sulfate from synoptic, need to look at much more data

NAMBLEX – most too early

- Add on to Jose and Roya's lab studies of new particle formation with diiodomethane in the presence of ozone and saw huge concentrations of particles
- Linked in an associated way to organic iodine emissions in the coastal zone
- Bell jar study of seaweed – particle production? Yes, over 1e6 particles/cc
- Mass spectrum contains many iodine and iodine oxide peaks, similar to Jose's, I2+ and I+ peaks are the largest
- James: didn't label anything he didn't know what it was, 56, especially, but saw that in Ireland too
- Could use help identifying 56, 58, and 100, one of them in the coarse mode

Discussion of UMIST data

- Eiko: question about differences in sulfate size distributions at Jungfraujoch
- Hugh: outside temp very cold, inside temp 20, both cloud and ?
- S-M Li: Brominated species in seaweed aerosols?
- James: soup of organics that came off, buried in a pile of other things
- Hugh: major peaks bigger than the air beam, never seen so much stuff in my life
- Evidence that the iodine particles are significantly nonspherical, we also ran the AMS in line with DMA, to size cut them, mass fragmentation pattern didn't change, but had effective density of 3-4, decreased the size cut of the DMA to 35 nm, saw AMS particles around 100 nm, below 30 nm w/ DMA, we lost all particles. Redo more carefully.
- Roya: low cut size? Used TSI nano DMA.

Alice: Prophet Data

- Remote site northern Michigan, pollution sources advected in
- Time trace from the entire period
- Two basic time periods: more polluted with southerly winds and cleaner time periods from North (Canada)
- Trends for entire study, scatter plots of organics vs. sulfate - correlated, ammonium vs. sulfate - correlated, nitrate vs. sulfate – not as well correlated, nitrate levels are very low
- Doug: the data set that we figured that all out on was Alice's
- John: would expect there to be a correlation?
- Alice: no, nitrate is iffy because sampling issues
- Doug: color by outside temperature, more remarkable was the organic to sulfate ratio was so well correlated

Southerly Flow

- Blow up of time trace, image plots show 400 nm mode in both sulfate and organics, with slightly higher sizes at the peak of the pollution episodes
- Sulfate is scaled down, organic peaks separated by m/z
- Average MS, full scale shows sulfate and 44 higher than 43, mix of stuff, delta =0? is dominant

Northerly Flow

- Time trend, image plot for sulfate, 300-400 nm mode and some times with a smaller mode
- Average mass spec shows the delta =0 and 2
- one spike in organic due to diesel truck

Small particle events

- Especially large event midday on 7/26/01
- Saw higher sulfate but not organics in the smaller particle mode
- DMA number distribution also shows event with growth of smaller particles
- Detail of size distributions for 3 events, distributions broad or with 2 modes
- Also had gas phase data

Elementary School in Denver

- Showed time trends, measuring off the roof of the school (2-story), not much in the nearby area
- Every other day (?), from midnight – 2 am increase in the organics
- Also day where there was a larger event
- Still going on, starting to look at this

Jon: Eddy Correlation with AMS

- End of Prophet, Aug 2-9 eddy flux from the top of the tower
- Aug 4, relatively low sulfate concentrations
- Needed to synchronize AMS and anemometer, triggered at 200 Hz, average for least 0.1 s
- Data load – would have needed $10ks of computer equipment for data! - figured out what needed to be saved and new format for saving it.

Prophet

- Sampled above the canopy from the top of the tower, no SMPS, no mixing
- Eddy correlation:
- Learning micrometeorology
- Calculate fluxes as a covariance with vertical wind speed
- Deposition velocity for each species, normalized for the number concentration
- E.g. 48 for sulfate

Sulfate Deposition with time

- Deposition velocities positive toward ground
- Looking at one day's worth data
- Pick best delay time between anemometer and AMS sampling times
- Noisy data in the afternoon with about 0.6 cm/s, 0 cm/s until about 10 am
- As f(size) don't believe this data because error bars are large
- Chopper 100 Hz, every 10 cycles,
- Also had size distributions, but huge amount of noise in that data, S/N ~1 for 1 s
- Goal was to look at nitrate deposition, but levels were really low, so weren't successful with that, have to look at other days
- Eiko: Forest? deciduous, topped trees as the forest grew
- Alice: Wasn't a lot of variation as a f(height), need to look at much faster time scales

Eiko: Current projects with AMS

- Micrometeorological flux measurements
- F(height) and combine with met measurements
- Eddy covariance
- Virtual disjunct eddy-covariance
- Fast sampling or sensor counting statistics important
- More masses/spend less time on each of them

New sampling mode

- Implement new mode to select certain masses and use MS mode to get better S/N
- Combine with light scattering probe later
- Deposition velocity – removal rate of particles by the ground, changes with size and time (Scotland OPC data)

Scottish Agricultural Grassland

- Change height manually using the same inlet, not very far because over grassland, simultaneous flux measurements of sensible and latent heat, CO2, NH3, N2O (CH4), height ~ 2.35-0.15 m
- Ammonium nitrate fertilization period may also be studied
- AMS housed in cabin

Data & Discussion

- Sulfate concentration, flux, deposition velocities as f(time of day) for three days
- Deposition velocities are reasonable numbers 2-8 mm/s
- Size dependence – need to average over long periods of time
- Deposition velocities as f(amu)! 35, 37 indicates emission!
- Jose: chlorine? James: not chloride
- Eiko: Emission gradients of HCl not far away, could be organic chloride, not inconceivable that it's seen
- Validate techniques with existing technology, ordered steam-jet aerosol collector, filter pack, optical particle counters
- Jon: Time?
- 50 minutes at each height, next time try 5 minutes, with automatic lifting
- Grassland deposition velocities are much lower than forest, moorland data even lower
- AMS not suitable for measuring fluxes at Edinburgh

Manjula: Mexico City

- Dara Salcedo – did most of the analysis
- Fixed sites and drove around the city
- Sources for most of the pollution is in the north, aerosol builds up in the southern part of the city
- Xalostoc, in the north, not a good site because lots of local sources, horrible smells (John), so not representative of Mexico City
- Pedregal, in the south, posh area, highest pollution there

Fragments

- Checked consistency of the data
- Nitrate: 30 vs. 46 linear relationship except for a few points with high organic loading
- Sulfate: colored by site, looks OK except deviation only seen increases in 64 at Xalostoc
- Everyone needs to look at it, make sure that fragmentation pattern is OK
- Chloride: fits 36/38 non sea salt chloride

Nitrate, Sulfate, Ammonium

- Predicted vs. calculated
- In general good agreement suggesting that ammonium was mostly neutralized, lots of XS ammonia in Mexico City

Time trends

- See a lot of nitrate in Pedregal in the afternoon, corresponds to when there is a lot of organic
- AAAR – Paul Ziemann talked about large alkenes can form alkyl nitrates easily, have to check this out
- Pedregal – aerosol mass loading correlate with photochemical markers (ARI, TDL instruments)
- Mobile lab drive around where we wanted

Speciated Size distributions

- During the day, see sulfate in the morning is in the large mode, in the afternoon see new mode growing in that goes away, also contains oxidized organics (44, marker), consistent display of large mode with sulfate and oxidized organic, processed mode during the day and small mode of organic
- Jose: similar to Houston
- But Mexico City aromatic precursors are not that high
- Jon: aerosol organic nitrates huge
- Doug: signature of ammonium nitrate, ammonia to sulfate+ nitrate balance worked well, 30/46 ratio also 3:1
- Jon: huge pulses of ammonia in California
- Jose: pulses of nitrate in the early morning (Atlanta), but here it goes into the aerosol because ammonia so high
- Manjula: lots of ammonia in Mexico City

Mobile Measurements – NYC Buses

- Try to get emission factors for various vehicles
- Measure CO2 and aerosol loading
- Nice correlation between them, measuring plume, emission index = loading of PM per ppmCO2
- Nice thing to cover a lot of vehicles and characterize under real world conditions, better than dynamometer

NYC mode

- Alternate TOF/MS every 2 s
- MS 6 spectra average
- TOF 6 masses, 1/3 s at each mass
- Diesel buses, unburned fuel + oil in the aerosol phase, ~ 2/3 particle loading associated with soot
- Size distributions averaged over event, mask out whole event to only look at the data you want
- Small mode organics (buses only), large mode sulfate (both buses and ambient)
- asphalt particles

Discussion

- James: Which masses? TOF 57, 69, 43, 44? 55, 83, 48, 64 (delta0, 2 + sulfate) and a high negative delta for aromatic (91 or 95)
- Mass spectra busy all over
- Johannes: was sulfate ever higher than organics? Uphill?
- No, pm sulfate was less than 0.01 microg ,m-3
- In Mexico City ambient sulfate loading goes down behind the truck!
- Johannes: catalysts?
- Some buses with NO-NO2 filter to trap particle, filter oxidized to clean, need to be careful about contamination from other plumes.

Roya: Twin Otter Studies

- Not much room!
- Velocity changes with ambient pressure, need to calibrate
- Sensitivity Corrections
- Lens pressure varies with sampling pressure – changes in the flow rate
- James: flow pressure in the lens of Differential Pressure gauge

Results from ACE-Asia

- AMS mass and DMA volume very well correlated except when dust levels were high, density about 1
- During dust periods, density (ratio) averages about 0.72
- Looked at back trajectories of air masses, some from Mongolia, China during dust events

Sulfate Layers

- As altitude increased saw sulfate concentration go down, after correcting to standard volume
- After converting to appropriate size at that altitude the distributions are very uniform
- When reporting mass concentrations, standardize the volume for aircraft measurements, but not for health effects.
- Report both?
- Should know/define the number
- 1 microg/m3 = 0.5 ppbv, with MW of 100
- See p.28 of Finlayson-Pitts book

ACE-Asia Results

- Vertical profiles of organics and sulfate
- Mixing state indicates some neutralization of sulfate
- Organics appeared in the same mode, missed whatever was below 100 nm
- Pie chart for contribution of different fragments to total organic mass, mostly oxygenated, but some aliphatic organics
- AMS vs. PILS (on C130), factor 2.5 for everything, correlation about 0.9 for sulfate, maybe due to impactor cut off, nitrate and ammonium also shown
- MOUDI on the wing of the twin Otter, run as a total filter, AMS had lower values for sulfate and nitrate
- Factor 1.4 for organic mass/OC mass
- Jose: at low concentrations may be seeing more mass
- James: R2 negative? Negative correlation? Don't know

Crystal-Face July 2002 Results

- Looked at developing convective systems
- CPC, CCN correlated with AMS spikes in organics and sulfate
- Image plots smaller mode increasing for sulfate around 100 nm, also see in DMA dry volume distribution at 50-60 nm mobility diameter
- Aerodynamic diameter estimated from DMA volume distribution is reasonable
- Still looking at the data
- Dave: difficult to explain the sulfate concentration was constant day to day, but organics weren't
- Roya: some of this may be noise (organics noisier)
- Jose: noise level for organics was 5 microg/m3, the lower layers were advecting from the surface, don't know what to make of those organic layers, may not be real, also spent some time sampling those layers so we may have better data

Discussion of image plots/Igor

- Doug: where does white come from at the bottom of the color scale?
- Jose: custom color scale to white out, James uses a white mask on the color scale
- James: short answer no, top parts of the distribution are closer together, so higher noise threshold
- Jose: suggestion on how to do it

Nobu: Ambient Sampling in Tokyo

- Group also does aircraft/balloon measurements of NOx and NOy
- AMS April 2002, only data from June this year
- Tokyo usually very hazy, sometimes in summer have a clear day
- Synoptic scale meteorology over Japan, Siberian high in winter from China over Korea
- Spring subtropical high from Indonesia
- Summer Pacific high

Local Met

- NOx concentrations in city
- Wind directions from sea during day, northerly at night
- U Tokyo near center of city, highway nearby
- AMS setup on 5th floor of the building, SS inlet tubing out the window, temporary, now have a better design for continuous measurements
- Simultaneous measurements not available during June, but now have them

Results

- Increases in mass loadings, probably due to traffic, during the early morning before sunrise (case1), mid morning (case2)
- Mass spectra very similar, need to do the delta analysis
- One big difference is the 44/43 ratio (case2 > case1)
- Distribution shifted to smaller diameter for case 1
- Separate masses, smaller particles primary emissions from traffic, fresh plumes, larger particles photochemically processed and probably internally mixed.
- Want to do continuous measurements of both gas and aerosols in Tokyo and hopefully aircraft sampling
- Two more groups are getting AMSs – NIES and JCAP, together better characterize spatial variation in Tokyo and Sea of Japan

Richard: Ship and Ambient Sampling

- Three projects:
- 1) Pacific 2001 (Vancouver)
- Filter nitrate and sulfate compared to AMS, nitrate reasonably good agreement, sulfate AMS slightly higher
- 2) C-SOLAS – Alcuma (Mexican) over Pacific Ocean, went northwest of Seattle in NE Pacific Ocean, dump iron into water and look at biological activity afterwards (Fe-limited), sulfur quantities, DMS (GC-MS), SO2, AMS plus DMA, nephelometer, PSAP, MOUDI, quartz filters EC/OC

SOLAS Results

- Time trend concentrations all less than 2 microg /m3, sulfate typically 1, much less for organics, ship plume, bow into wind, sometimes had exhaust in sampling lines
- DMA volume multiplied by 1.78 remarkable agreement with AMS, sampling right next to AMS, same inlet
- Mass distribution for sulfate constant through out project
- Organics/SO4 fairly constant except during exhaust sampling
- Jose: cutoff in the lens?
- Didn't look at transmission
- Johannes: compare with DMA data, but only up to 300 nm geometric diameter
- T = 550 C
- Jose: evaporation losses in inlet?
- Outside, copper, room temperature differential not always the same direction.
- Jose: try scanning DMA up to higher masses
- Ann: steeper cutoff with new inlet?
- Doug: better transmission of larger particles when the smaller cut point is moved up from 40-60 nm, might be seeing a measurable effect,
- Jose: try switching 100 micron orifice with 120 micron orifice

3) Egbert

- Ambient Sampling in Canada
- Gas phase and aerosol instrumentation
- Time trend, mass loadings dominated by events with diurnal cycles of nitrate early on, later sulfate events
- Comparison with TEOM & nephelometer, everything co-varies, but TEOM mass is substantially more than AMS, look at how the data are processed with James' program
- Correction factors as in the program: 1, 2.5, 0.7
- Close up of one high TEOM event, after fog at night with high levels of NOx, oxidation of NO2 with O3 at night producing particulate nitrate (NO3 or N2O5), lots of ammonium in the region, ammonium nitrate in the aerosol

Qi: Pittsburgh Supersite

- North edge of CMU – PAQS
- Characterize Pittsburgh PM, quantify sources, evaluate new PM techniques
- Sept 7-22, 2002 with G1 AMS
- Time trends – use NR for Non-refractory
- Clean air from Canada, dirty air also seen
- Sulfate is the dominant component, then organics, nitrate is low

Results

- Size distributions all on the same y-scale
- Put all the plots for each day for each species
- Increases in peak size, bimodal to monomodal, chose 4 typical days (24 hr averaged) that clearly show the two modes.
- Clean days dominated by small mode, polluted days with the larger mode, distribution shapes mostly similar for the different components
- Comparison with SMPS, indication of nucleation in SMPS, trimodal distribution in the morning of Sept.12, similar size range for each mode
- Peak in surface area seen at the same time

Results & Discussion

- MOUDI comparison – July 2001 with Sept 2002, looks very good for the distribution of sulfate, ammonium and total
- James: MOUDI normalized to dlogDp space? Yes?
- Eiko: cutoff in AMS also seen with MOUDI
- S-M Li: need to plot in the same way
- Hugh: ultrafine nucleation? Yes, volume convolved
- Doug: number density plot looks the same
- Jose: volume concentration cut off around 10 nm
- Eiko: AMS measures stuff growing on small particles, not nucleation
- Hugh: volume collapsing around 9 am, breakdown of nocturnal boundary layer
- Jose: cartoon of event, plume of SO2 above, depletion of ammonium and SO2 at the same time, growth of particles, but also nucleate in parallel
- Size distribution before and during nucleation event on Sept 12
- Growth of sulfate in fine mode
- Particles before were organic, within detection limit organics are not growing in the smaller mode
- Doug: organics are the remnant of the traffic mode
- Hugh: prediction based on the breakdown of the nocturnal boundary layer
- Doug: this is predicted the night before, based on the weather, every 3 days or so
- Jose: lots of SO2 everywhere.
- James: sulfate in the low diameter mode instead of his measurements
- Hugh: sulfate levels are much higher in Pittsburgh
- Hugh: accumulation mode is regionally dominated
- Doug: standardize total on every plot

Johannes: HAZE

- Hohenpeissenberg – mountain in Germany 1000 m, surrounding mountains 300 m below, May 2002
- Nucleation events sometimes observed there, but not during the time they were there (2-3 per year, not like Pittsburgh)
- List of measurements, project not funded, hasn't seen any other data
- See Alps during clear days
- Aerosol inlet outside

Results & Discussion

- Time trends
- Sharp cutoffs after rainy days
- During the day, nitrate and organics have similar slope except where nitrate shoots up
- After rain, nitrate didn't change the same way as the rest of the species
- Need to look in more detail

More HAZE Results

- Image plots, size distributions messed up during rain, any ideas
- Doug: mass 18? No
- Ann: look at the complete picture when it rains, WD and other gases because could be change in the air mass, not always changes in aerosol due to rain itself
- James: distribution also drops out after rainy period, might be particles creeping into the second DC region
- John: several micron size hard to get in that lens
- Doug: hunch these are water particles,
- Doug: as soon as you see a region where it doesn't make sense plot the size distribution, look at the raw data in TOF, mainly to make sure its working properly
- Jose: red spikes (spots) with green around it, symptom of noisy data, inlet T and RH compare to outside and see if you might have condensation in the inlet by calculating dew point or water vapor concentration
- Pie charts for days with/without rain
- Higher nitrate concentration on rainy days

Falcon deployment

- In March 2003 up to 12000 m
- Configuration with CO2, tandem DMA, and MS (Arnold)
- Removed 80/20 and built own rack with the quad upside down, inlet sticks out into the next rack
- Maybe add UPS and particle counter

Jay: Harvard Forest, BC, Whiteface Mtn., Summer 2002

- Harvard Forest:
- Time trace shows big variations in mass loadings
- diurnal patterns in the various species, see big peak in sulfate in the afternoon
- Back trajectories for large sulfate, looks like long range transport for Aug 20
- Other back trajectories also produce single mode at 500 nm with all the species internally mixed
- Manjula: DC offset for sulfate not set right? Yes
- Manjula: Issue for the logging software after EM cal
- Trajectories with a Boston source, organic and sulfate strong, but offset from the other size distributions
- James: back trajectories all coming from too close to the surface
- Jose: high side on the sulfate tails more than the other species, look at the single particle pulses and invert the data
- Doug: large particle mass for sulfate is counted, take out the tail by adding the single particle pulses when they appear, remember that high particle side means spread out in the distribution
- Jose: calibrate with ammonium sulfate, sulfate shifted compared to ammonium, similar with something less volatile

BC Results & Discussion

- BC: 2nd floor window
- Sulfate events were much smaller than observed at Harvard Forest, systematic error in collection or real
- Higher loadings of organics than sulfate compared to Harvard Forest
- Most of the high sulfate/organic events with air from the SW
- Back trajectories on Aug 12, long range transport from eastern seaboard (Washington, NYC)
- Organic dominated events (Aug 4) air from Canada, then sitting around Salem area, size distribution shows higher loading for organics, with relatively more in the smaller size range
- Doug: this instrument has a much larger air beam than the others, the ammonium tail at the low sizes is from the air beam and can actually subtract this out, be aware of that!
- Jay: computer crashes, new computer had more noise after July 25
- Doug: this instrument is serial #0
- Jose: don't clip zeros, indicate noise level, for ammonia, look at 16 TOF other than the AB
- Hugh: block average some periods? Smoothing?
- Jose: bring the rest down, artificial
- Hugh: all data +/- sigma, amount of time spent with 2 sigma attached, the best thing is to plot the negatives
- Johannes: show error limits, should be above zero when included, especially for databases.
- Jose: report as they are, noisy data
- S-M Li: real world there's no noise, so need to filter out
- Johannes: averaging but cannot remove it
- Hugh: how to present final form and present in graph? Need to put negatives into the database. Say what you've done for a plot.
- Jose: don't have the real concentrations, some instruments remove zero and bias instruments, that's completely wrong.

Hacene: Source Characterization

- Incinerators, aircraft, ammunition sources
- Very high mass loadings, hard to sample, clog orifice, AMS sensitivity too high, spectrum different from ambient
- Boeing 757 results
- Total organic carbon as f(distance from engine, engine power), spikes when switching from idle to on and on to idle, takes ~8 minutes to get back to background conditions, real spikes up to 40 mg/m3
- 85, 113, 127, 155 peaks in MS, different populations, transient period has both fuel and oil, steady conditions just oil?
- Emission index as f(distance), for sulfate and organics they increase
- Size distributions shift to larger masses at longer distance, but organics shift up larger than sulfate, look internally mixed at short distances, definitely not at long distances
- How is Da affected by AMS flow rate? Errors in flow rate are magnified in aerodynamic diameter.

Other experiments

- Ammunitions propellant
- List of compounds present
- Mass loadings 3-4 orders of magnitude higher than ambient air
- Oven temperature ramping, saw “sulfate” increase at higher temperature, additional peaks due to zinc and other metals, Zn has isotopes at 64, 66, 68, correct spectrum for zinc contribution
- Organic decreased while 44 increased with time
- Doug: green is not really organic

Other Experiments, contd.

- SS incinerator, Manchester
- Still need to correct for all the variation in oven temperature, flow rate
- Vary many parameters just hoping to understand what is going on there
- Every time you increase the temperature of the oven, the total organics increase, then go down, need to let it stabilized and then get the measurement.
- Doug: size distributions can show prediction of when it will plateau, sharpens up because vaporizing all of it
- E.g., 64 gets sharper and sharper at higher temperatures
- Better to decrease the emission current and keep the EM voltage the same to decrease the sensitivity when the mass spectrum gets saturated

Discussion

- James: degassing from the oven should get subtracted out when you take the difference spectrum
- Doug: background has a ramp on it so that it's changing with time, systematic change on the wrong time scale, changing quickly, 0.2 Hz average against things that are faster than that
- Jose: can only measure times scales that are faster
- Doug: account for that ramp if you just assume … whole other level of analysis
- Calculate the organic?
- Doug: turn the oven back down, have to keep ramping oven up and down and reach steady state.
- One way to solve all this, the biggest problem is clogging the orifice, need to dilute the sample, can we dilute the sample quantitatively, even still using a cyclone.
- Doug: showed the blow up of the 757, more efficient (less organic aerosol mass) at higher engine powers after dividing by CO2, sulfate showed no difference.
- More refractory compounds vaporize at higher temperatures, all mineral sulfate, not ammonium, ambient sampling no idea how important refractory materials are, colder temperatures, we might change the fragmentation pattern for organics, but have to do it, systematically in the ambient, 1 minute transition, 5 minutes at new temperature, then transition again.
- Organic signals decrease, but subtraction problem, which can be fixed, we have to do it and find out how practical it is.
- Water content was very high, but for the first one it was very low (wet scrubber) after that used a compressor, dew point 150 C, heated inlet line to 150 C, water condensation went away.

Johannes: Diesel Exhaust

- Particle filters put on exhaust
- Primary vs. secondary – secondary may not be removed
- Low power settings – soot particles
- Fuel sulfur emitted as SO2
- High power converts SO2 to SO3 – sulfate which condenses on soot or forms new particles
- New (30 nm) particles composed of H2SO4/H2O?

Diesel Experiments

- All experiments at Achen are for diesels, gasoline studies in the US
- Showed setup
- Mechanical rotating diluter, 2-3 sampling lines
- James: size range measured? 10 nm – 1000 nm
- The problem: mass calibration was off
- Balzers control menu, not their problem
- National Instruments fast board output voltage ~ factor of 2.1
- Couldn't correct mass scale by AMS software
- Manjula: high mass?
- Johannes: I tried everything!

Results

- Varying fuel content, power loadings, looked at size distributions with SMPS
- Took two 20-min samples to make sure conditions were stable
- Higher speed, higher particle production
- More S-content, more sulfate
- SMPS comparisons, they might have had a problem
- Thomas: Need to check that there are 0 particles at 0 voltage, multiplied by a thousand, fix it by changing the operating up end.
- Hugh: high concentrations at low voltages, need to be very skeptical exactly for that reason
- Still took measurements with AMS

AMS results

- For the same S content, same speed:
- Low power, see organic pattern with very low sulfate
- High power see organic pattern with very high sulfate
- Catalyst designed to reduce NOx
- ARI: see different results
- Doug: Different technology than anything we've sampled. Conversion efficiency?
- Johannes: haven't made quantitative calculations.
- Doug: mass 81 is still smaller than 48 and 64, pure sulfuric acid shows mass 81 larger, water distribution is from sulfate decomposition (H2SO4 to H2O+SO3)
- John: Need more organic masses programmed there, to show what else with the large mode water
- Doug: pure water at large mode
- John: catalyst temperature studies? No
- Where is the sulfur? With more S-content, don't see a quantitative increase
- Size distribution very similar to SMPS for high S-content, high power – 100% transmission efficiency
- Doug: Dilute by factor of 100, what does that do to the water?
- "nucleation" particles only observed after a cold start, but too much noise in the size distribution

Jay: water uptake by Soot

- Flame source, dry, DMA, condense H2SO4 (don't see sulfuric acid nucleation), then H2O (future control), (future t-controlled inlet), then AMS
- AMS shows changes to the particle size distribution (m/z 202 shown)
- No uptake w/o H2SO4
- Measure H2SO4 condensed with AMS, physically increase particles in size and also in density.
- Density factor when adding water, hard to quantify addition of water
- Use MS to do it. See carbon backbone of soot and poly-aromatic functional groups (doubly charged ions), with H2SO4 see 81 is the largest, this sulfate is not entirely pure sulfuric acid, and 81 is a lot bigger when it is pure.
- Effect of H2SO4 loading on water uptake of activated soot – with more sulfuric acid, get more water
- Thomas: why isn't there an increase for the magenta data, slight decrease (intermediate sulfate)?
- Water evaporation in the AMS inlet. And didn't go to high enough RH. In between 50-75% water loss, compared to predicted from vapor pressure of water.
- Doug: fragmentation pattern, pure sulfuric acid has less(?) water than ammonium sulfate – need to look at quantitatively. Propane soot – effective density of 1.2, dirty propane – effective density more like 1, distributions like Johannes showed.

Melissa: Tholins

- Couple billion years ago (BYA) = early earth
- Geologic record indicates that molecular oxygen was present 2.4-2.2 BYA
- Solar intensity much lower than today
- Larger greenhouse effect, otherwise temperature too low for liquid water
- Moderate levels of methane and ammonia would increase temperature, but they would be destroyed “rapidly”

Titan as a model

- P=1.5x earth
- N2, CH4, haze formation due to photochemistry
- Radical initiation ultimately forms polymers. Monomer particles <0.5 microns.
- Photolysis of CO2 forms O atoms could stop the polymerization of CH4.

Why use AMS?

- Morphology or composition changes during collection – want real time, in situ analysis method – AMS
- Lower pressure than atmosphere, size calibration. Try working at constant pressure.
- Initial results w/o CO2 – complex mixtures of organics, 27, 28, peaks separated by 14 amu, delta analysis
- 77, 91, 105 aromatic species
- Size distribution is uniform, internal mixtures of various organics
- Increased amount of CO2 – C/O smaller, large peak at 58, 44, 72, 84, 86, and 97
- More CO2 – smallest C/O, lower total signal, higher masses aren't present
- 58 peak increases and decreases as CO2 increased
- For similar conditions, AMS 60-70 nm, SMPS 200 nm, shape and density affects
- High accuracy MS to aid in identification 0.005 amu accuracy, could identify species based on isotopes
- Early Earth Haze Aerosols
- Manjula: 58 cuts the carbon chain formation, gets smaller and smaller
- David: Electric discharge produces ions, UV produces radicals, lightning shock waves cause thermal chemistry, different results from different energy sources.

Doug: Upgrade Options

- Inlet RH, P & T at the inlet
  - Older versions add lens P for inlet flow measure
- IS420 ionizer control upgrade/compact ionizer
- High throughput lens? Requires V301 and likely Alcatel (next three months)
- Moveable wire
- Inlet T(RH) control
- Filter switching?? need systematic background correction
- Light-scattering module – more science for aerosol measurements

Future operational issues

- Heater temperature variations 300, 600, 1000 C
- Inlet temperature variations 5 – 30 C, RH 20 or 30 % to 100%
- Moveable wire – beam divergence
- Random (automatic) in line filter switching
- Analysis software development
- Save every minute – HDF
- Accumulate averages over 3 dimensions above
- Light scattering probe of single particles (> 100 nm)

TOF Size Distribution Masses

- Background 11
- Air beam 28 (32)
- NH3, H2O 16, 18
- NO3 30, 46
- SO4 48, 64, 80/81?
- Org 43, 44, 55, 57, 53 (delta-2), 45
- Aromatic 77 (91, 105)
- Cl 35, 36
- Check S/N in other peaks 85 (suddenly appeared in Alice's data)
- Wish list for adding peaks automatically into data acquisition program – Manjula already there

Discussion

- Jose: bottom of the MS window biggest peaks
- Johannes: set automatically in F6 window
- Doug: another column in the F6 window, that sort of software control is dangerous, but maybe practical
- Manjula: 67, 79, 91, but 55 may have more contribution from photochemical than 67, etc.
- Choose as many inorganic masses as organic masses, which have more S/N than the inorganics
- S-M Li: sulfate fragmentation pattern known well, save space for other ions?
- Plausible idea, save ratios in the mass spec, 48 best S/N, not out of the question to just use 48
- Jose: disagree, interferences, maybe get rid of 64
- Manjula: larger mass on the delta 2 scale, photochemical events have short chain, higher mass more distinct and only from combustion
- James: 57 is more shifted towards the lower mode than 55, but further up get the same sort of ratio, but have to check.
- Jose: 71 is shifted more toward smaller mode
- Manjula: even go up to 95
- Jose: more S/N at higher masses
- James: background is really bad at 44
- Jose: watch the fluorine peaks (19?, 50, 69, 100, 119, 150, 169, 285 is the high one)
- James: may have other peaks from other pump oils
- Phil: masses to use if see fire 60 (major peak from levoglucosan)

Number of Masses to Scan

- 2.5 MHz ~ 30 masses
- Play with it and see when it crashes, do it before you go to the field, wait for two saves (page lock error)
- Put shortcut onto desktop with automatic start in alternate mode to get program to start after crashing, John suggested …
- S-M Li: Prevent automatic startup when no one is there, pumping on
- Doug: get UPS that won't turn back on again
- Jose: UPS turn off computer
- Eiko: RCDs if they loose power, they stay off
- Jose: system is robust, filaments protected, background increases, automatic valve that is not hot or little channels that loose particles, need compressed air for pneumatic valve
- S-M Li: ball valve?

Next AMS Users Meeting

- Oct. 26 – 28, 2003 at Aerodyne (Sun- Tues) (AAAR Oct 20-24 in Anaheim)
- Format?
- Doug: keep the structure of this meeting identical, with update on hardware and software, then scientific issues and results, training issues are separate one
- Training students in April? People are interested.
- Doug: driven by new orders, we would determine the schedule, but open it up to anyone, not just new users, likely necessary
- John: vote on presentations for viewing
- Hugh: no time for posters, point to bring people together, common areas submit overheads to a single speaker – summary of what people have done